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Pilot Constructed Treatment Wetland and Natural Media Filter

Clint Swires
University of Tennessee - Knoxville

To the Graduate Council:

I am submitting herewith a thesis written by Clint Swires entitled "Pilot Constructed Treatment Wetland and Natural Media Filter." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

Randall W. Gentry, Major Professor

We have read this thesis and recommend its acceptance:

Chris D. Cox, Qiang He

Accepted for the Council:
Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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Carolyn R. Hodges
Vice Provost and Dean of the Graduate School

Pilot Constructed Treatment Wetland and Natural Media Filter

A Thesis Presented for
The Master of Science
Degree
The University of Tennessee, Knoxville

Clint Swires
April 2009

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ABSTRACT

A Natural Media Filter (NMF) and Constructed Treatment Wetland (CTW) pilot study was performed on an industrial landfill leachate site. The pilot study was designed to test if a NMF and CTW could be a low cost replacement option for the current wastewater treatment system. The main contaminates of concern for the leachate were poly-chlorinated biphenyls (PCBs) and ammonia.

The pilot unit consisted of two systems, a subsurface flow CTW and an up-flow NMF that utilize mushroom compost as a media. The two units were run in parallel and were both supplied with untreated leachate. The CTW was operated at a flow rate of 0.3 gpm with a 2.2 day retention time. The goal of the study was to operate the NMF at 0.2 gpm with a half-day retention time, but due to operational issues this flow rate varied throughout the study. The Influent concentration of ammonia varied from non-detectable to 17 mg/l as nitrogen, with effluent concentration from the CTW fluctuating from non-detectable to 16 mg/l. For PCBs, influent concentrations during the majority of the study were non detectable, but during the last few months of the study large spikes in PCBs were recorded. The natural media filter was able to remove PCBs below limits of detection for most of the study, but breakthrough occurred towards the end of the study.

For the constructed treatment wetland, removal of ammonia and nitrate/nitrite were modeled using the both the Plug Flow Model and the Tank-in-Series Model. The CTW was considered to be a Plug Flow unit and was oxygen limited. For the Natural Media Filter, the data collected did not allow for a proper evaluation of the adsorption capacity of the unit. A PCB mass balance was performed on the NMF from data collected from core samples of the compost. The unit was successful in removing PCB

loading nine times higher than its designed capacity and the failure of the unit is attributed to short circuiting caused by the unit freezing.

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CHAPTER I
INTRODUCTION AND GENERAL INFORMATION

Since the Clean Water Act of 1972, industry and government have made many strides to reduce the affect manufacturing has on the environment. Research by both private and public organizations has continued to expand both our knowledge of pollution and our ability to treat pollution. For industry managing, treating and reducing pollution has become an everyday part of business, but with a financial cost. As discharge limits become more stringent and sampling methods become more accurate industry continues to push for new, lower cost technologies. As cost controls become more important, companies are starting to look more at low maintenance systems such as constructed treatment wetlands (CTW) and natural media filters (NMF) to treat wastewater. These systems require low maintenance, have a low installation cost, and can be very efficient at treating low levels of contamination in wastewater streams.

Alcoa Inc. is one of the world's largest manufactures of aluminum and has been in business for over 100 years. Through its research group, Alcoa Inc. has continued to look for ways to implement new technologies and reduce its effect on the environment. The Alcoa Environmental Health and Safety (EHS) Technology Group has done extensive research into the development of NMFs and has started to couple this technology with CTWs. These two technologies have shown excellent potential at being both highly affective and low cost. They have also indicated their long term sustainability with minimal maintenance needs. The Alcoa EHS Technology Group has continued working with many Alcoa locations to implement this technology while meeting discharge limits and providing cost reduction compared to standard treatment technologies.

In Alcoa, Tennessee Alcoa Inc. operates an aluminum rolling mill, Tennessee Operations (TN Ops) North Plant, which has been operating since 1941. Like many facilities of its age and size, the Alcoa North Plant has legacy issues it must continentally manage to insure its compliance with government regulations. The Alcoa North Plant operates a landfill leachate collection pond and wastewater treatment plant at its National Pollution Discharge Elimination System, (NPDES) permitted Outfall 007. In 2007 Alcoa Inc. North Plant Environmental Department started investigating possible replacement systems for the current mechanical system. The two major contaminants of concern at Outfall 007 were PCBs and ammonia. Alcoa EHS Technology Group in coordination with location environmental engineer Clint Swires proposed installing a pilot NMF and CTW to test its applicability as a full scale replacement option.

Alcoa EHS Technology Group had success with this technology at other Alcoa locations and was interested in continuing the research. For privacy purposes the location of the facilities that have utilized this research will not be mentioned and only referred to with their Alcoa initials. The original focus of the pilot study was to determine if natural media filtration could remove the PCB contamination form the leachate. After start up of the NMF, a subsurface flow CTW was installed in parallel to the NMF to remove ammonia from the leachate. The NMF was started in March of 2007, with the CTW being installed in May of 2007. The unit was run until March of 2008 when study was discontinued due to lack of funding.

Data gained from previous pilot studies performed by the Alcoa EHS Technology Group was used to design the NMF and commercially available mushroom compost was used as the filter media. The CTW was designed using standard design equations and a subsurface wetland was chosen to discourage wildlife habitation. Leachate was pumped directly from the leachate collection pond into each unit at varying flow rates. The units were continually operated during the length of the study and were exposed to ambient weather conditions. Sampling performed on the unit was focused on monitoring the technologies ability to remove the contaminates of concern and to identify other changes in water quality caused by the pilot units.

The purpose of this pilot study was to test and evaluate a NMF with a CTW to treat the leachate at Outfall 007. Alcoa Tennessee Operations was investigating replacement options for its wastewater treatment system at Outfall 007 and the location presented an ideal situation to test this technology. Alcoa Inc. has not completed a final report on the pilot unit and the results of the study have only been used to determine future options for this technology. A literature search was performed to better understand and evaluate the data gain from this pilot study. Critical assessments and conclusions were determined from the evaluation of the data collected during this pilot study.

CHAPTER II
LITERATURE REVIEW

A. Constructed Treatment Wetland Overview

The ability of natural wetlands to improve water quality has been recognized for many years. Wetlands are very effective at removing pollutants such as organic matter, suspended solids, metals and excess nutrients from water streams. The pollutants can either be removed mechanically by sedimentation or by natural filtration. The pollutants may also be removed by chemical reactions or biological decomposition where the pollutants are transformed from complex compounds into simpler compounds that can be taken up by plants or other biological matter. These nutrients are utilized by both plants and biological matter for biomass production. Constructed treatment wetlands (CTW) utilize the same mechanisms as natural wetlands for pollutant removal, but engineering principals have been applied to their design to produce a controlled, predictable system for pollutant removal. (Hammer 1989)

CTWs are defined by the U.S. Environmental Protection Agency as wastewater treatment systems that rely on physical, chemical, and biological processes typically found in natural wetlands to treat a relatively constant flow of wastewater. CTWs can either be free water surface (FWS), where there is an open water surface above the saturated media or subsurface flow (SSF), where there is no open water surface and the water level is kept below the surface of the media. For both surface and subsurface wetlands the water level is typically less than one meter or three feet. The media is typically gravel of different sizes; with larger gravel being near the bottom of the wetland

and fine gravel being near the water surface. The larger gravel provides porous areas for microbial growth to attach to whereas the fine gravel provides a media for plant growth and roots. Typically cattails and bulrush are the plants that are used in CTWs. In some cases peat-moss or another hydraulic soil may also be utilized as a media for plant growth near the upper portions of a wetland. Flow through constructed wetlands is typically horizontal and have retention times in the 2 – 10 day range. (EPA 2000)

CTWs have typically been used in agricultural wastewater treatment and polishing units for municipal wastewater treatment. CTWs can be very effective at removing biological oxygen demand (BOD), ammonia, phosphorous and other nutrients. Engineers have now started to utilize CTWs for passive treatment of industrial wastewater, acid mine drainage and landfill leachate. (Moshiri 1993)

B. Constructed Treatment Wetlands for Landfill Leachate Treatment

Landfill leachate typically has high concentrations of ammonia, nutrients, and chemical oxygen demand (COD). Other pollutants such as metals and organics may be present in the leachate, but at moderate levels. Leachate flows are typically low compared to municipal or industrial process wastewater flows and range from 10 to 10,000 gal/day. This design criteria has made constructed wetlands, both sub-surface and surface flow, a valuable and increasing option for treating landfill leachate. Since the late 1970's, CTWs have been successful at treating leachate at locations in New York, Indiana, Florida, Norway, British Columbia, and the United Kingdom. This ecotechnology has been increasing in use because of it relatively low cost compared to other alternatives and its long term effectiveness at treating landfill leachate. (Mulamootil, 1999).

Typical methods for treating landfill leachate consist of pumping and hauling, forcemain, or installation of an onsite mechanical wastewater treatment system. Pumping and hauling is where leachate is pumped and then hauled to an offsite mechanical wastewater treatment facility. In a forcemain system the leachate collection system is piped directly into the local municipal wastewater system. Sharon Rew and George Mulamoottil performed a cost comparison of leachate treatment technologies for a typical municipal landfill and presented it in the book Constructed Wetlands for the Treatment of Landfill Leachate. The landfill consisted of 219 hectares and was opened in 1980. The landfill had a design capacity of 11,800,000 m^3 and was permitted to receive domestic, commercial and non-hazardous industrial waste. At the time of the cost comparison the landfill was predicted to be active until 2030 and the leachate was being pumped and hauled to local municipal wastewater treatment plant. Three treatment technologies were evaluated during the cost comparison, pump and haul, forcemain, and CTW. The cost comparison revealed that a CTW had a capital cost 97% less than the forcemain and that its annual operation cost 62 to 98% less than that of the other options. Table 1 is a summary of the cost comparison.

Even though a landfill is closed it will still produce leachate and the leachate will still need to be treated before release. CTWs offer an advantage over traditional treatment systems because of their longevity. Most CTW require very little maintenance and will

Table 1: CTW Cost Comparison

Cost	Pump and Haul	Forcemain System		Constructed Wetland	
	Current	Low	High	Low	High
Capital	NA	$2,000,000	$3,500,000	$37,000	$74,000
Annual Operation and Maintenance	$40,000	$20,000	$34,000	$5,000	$50,000
Annual Treatment	$130,000	$99,000	$99,000	$0	$0
Total Annual	$170,000	$119,000	$133,000	$5,000	$50,000

passively treat leachate for years.The longevity of a CTW is increased by is flexibility to treat different pollutants. If changes in the landfill cause a new pollutant to become a contaminate of concern, a traditional chemical or physical treatment system may not be able to remove that pollutant. For example, air stripping is very affective at removing ammonia but has no capability to remove metals. A CTW has the ability to remove both pollutants and fluctuate with variations in the landfill leachate. Though CTWs are land intensive; the low flows of landfill leachate and buffer space surrounding landfills do make them a valuable option for leachate treatment.

CTWs are classified as a passive treatment system which can create challenges that limit their usage at landfills. CTWs are usually not able to produce high purity effluent streams and stringent effluent guidelines may not be achieved if the influent concentrations are too high. Problems with treatment efficiencies can also arise from the preferential flow channels that form in wetlands. These channels will allow leachate to pass through the wetland in a time less than the designed retention time. Stochastic effects will also limit the efficiency of a CTW because they are a natural system. These stochastic effects include biological factors like insect attacks on the plants in the wetlands, seasonal change or climate limitation on biological activity, and extreme changes in influent flow volumes such as droughts and floods. A major concern of wetlands is the bioaccumulation of pollutants that may occur in the flora and fauna that is present in the wetland. This bioaccumulation can produce unintentional biohazards that threaten public health. All landfill leachate will have different characteristics and each constructed wetland will have a different performance. Proper design, testing and research of similar applications can help to address the limitations of constructed wetlands as a treatment option for landfill leachate. (Mulamootil, 1999)

C. Ammonia Removal in Constructed Treatment Wetlands

Due to its toxicity, ammonia is often a regulated nitrogen species. In CTWs ammonia is often an intermediate in the processing of nitrogen. It can be produced by the ammonification of organic nitrogen in CTWs or processed thru aerobic processes. Some research also suggests that ammonia may be oxidized thru anaerobic processes in CTWs. The removal of ammonia from wetlands is greatly affected by the biological processes in the wetlands. Decaying vegetation and biomass can increase the total nitrogen in the wetland. In some case effluent ammonia can be greater than influent do to ammonification. (Kadlec and Walace, 2009) Oxygen availability, hydraulic loading rates (HLR), temperature, wetland types, and influent characteristics can have a large affect on the fate of nitrogen and in-turn the removal of ammonia by constructed wetlands. (EPA, 2000)

In most wastewater treatment systems, ammonia is removed through microbial nitrification. This process is also the primary removal system for ammonia reduction in CTWs. In CTWs, especially in subsurface wetlands, uptake of ammonia can also occur during biomass production. In Kadlec and Wallace's book, Treatment Wetlands, case studies indicate that biomass grows at 2000 g/m^2-yr and that the biomass tissue contains two percent nitrogen, accounting for 40 g/m^2-yr of nitrogen uptake. In 117 case studies of subsurface wetlands performed by Kadlec and Wallace, plant uptake constitutes for nearly a quarter of the annual nitrification rate. These studies indicate that the amount of ammonia consumed during biomass production can have a significant impact on the overall ammonia processing in the wetland when influent ammonia levels are less than 120 g/m^2-yr as nitrogen. Kadlec and Wallace also suggest that designers should consider that as biomass decomposes nearly ninety percent of the ammonia consumed during biomass production is release back into the water column.

The classical theory for removal of ammonia in constructed wetlands is through autotrophic nitrification and that 4.6 grams of oxygen will be needed to nitrify every gram of ammonia as nitrogen, 4.3 grams of oxygen for nitrification and 0.3 grams for microbial use. This theory does not account for the ammonia removal due to biomass uptake and must be coupled with BOD removal to determine the proper amount of oxygen demand. subsurface wetlands are assumed to be oxygen limited systems and studies indicate that microbial process in these systems may be closely linked through co-metabolic processes. This co-metabolic process may provide alternate pathways for ammonia removal such as anaerobic ammonium oxidation or the utilization of ammonia as an energy source for heterotrophic organisms. If the stoichiometery of an alternate ammonia removal process is considered, the oxygen need for ammonia removal is greatly reduced as indicated by Table 2.

The availability of oxygen in a subsurface wetland will determine what process, classical or alternative path, will be the dominate ammonia removal process. Though it is highly debated on how it is supplied into a subsurface wetland, through plant oxygenation or atmospheric aeration, it is agreed that the oxygen naturally transferred

Table 2: Oxygen Usage in SSF Wetlands as a function of Stoichiometry of BOD Reduction and Ammonia

Precentile	BODLR[a] (gO/m^2*d)	Internal ALR[b] (gN/m^2*d)	External ALR[b] (gN/m^2*d)	Maximum[c] O Usage (gO/m^2*d)	Intermediate[c] O Usage (gO/m^2*d)	Minimum[c] O Usage (gO/m^2*d)
0.05	0.36	-0.01	-0.14	0.9	0.6	0
0.1	0.72	0.05	-0.04	2.1	1.2	0.2
0.2	1.11	0.11	0.01	3.6	1.7	0.4
0.3	1.4	0.15	0.14	4.2	2.2	6
0.4	1.88	0.2	0.24	5.2	2.7	0.8
0.5	2.17	0.23	0.28	6.3	3.2	1
0.6	2.93	0.29	0.38	8.5	4.4	1.2
0.7	4.22	0.35	0.57	10.6	5.4	1.5
0.8	5.28	0.47	0.73	12.8	7.5	2
0.9	10.58	0.63	1.09	21.1	12.8	2.6
0.95	18.54	0.78	1.52	38.2	23	3.6

Note: Both internal (from organic N) and external ammonia loads are considered. The Anammox rout requires hal the ammonia to be converted to nitrite, which needs approximately 1.7 gO/gN. BOD may be reduced by anaerobic or aerobic processes the data represents 85 wetlands and 168 wetland - years of data.

[a]BODLR = BOD load removed

[b]ALR = ammonia load removed

[c] the maximum case assumes 1.5 gO/gBOD and 4.6 gO/gNH_4-N

the intermediate case assumes 1.0 gO/gBOD and 1.7 gO/gNH_4-N

the minimum case assumes 0.0 gO/gBOD and 1.7 gO/gNH_4-N into wetlands is 7.5 to 6.8 g/m^3-d. A subsurface wetland is usually divided into an aerated and an anoxic zone. Figure (2.1) shows the different anoxic and aerated zone in a subsurface wetland and how oxygen in transferred into a wetland. (Kadlec and Wallace, 2009)

In early studies of pollutant removal in constructed wetlands it was assumed the system was a Plug Flow System and the removal could be modeled using first order Plug Flow Model, Equation (2.1). (Hammer, 1993)

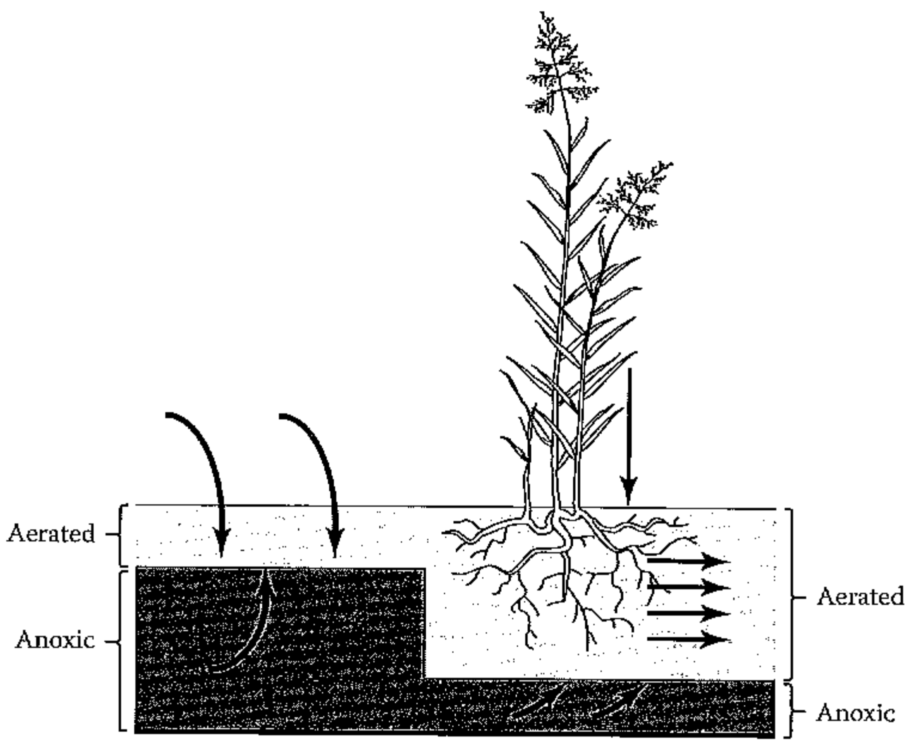


Figure (2.1) Oxygen Zones in SSF Wetlands

Plug Flow Model

$$k = q\ln\left(\frac{C_i}{C_o}\right) \qquad \textbf{(2.1)}$$

Where:
k = first order removal constant , m/d
q = hydraulic loading rate, m/d
C_i= Influent Concentration, mg/L
C_o= Effluent Concentration, mg/L

Kadlec and Wallace suggest that there are many “pitfalls” in using this model due to its dependency on regressions of data plots. If average first order removal constants are determined from these regressions and used to determine effluent concentrations the results vary greatly compared to observed data. The reasoning for this failure for the model to predict effluent concentrations is that CTWs do not operate as plug flow system. Kadlec and Wallace agree with the early studies of CTWs that pollutant removal is first order but suggest that other models should be implemented into design equations.

Kadlec and Wallace suggest that CTWs can be better modeled using the TIS Model or Tank – In – Series Model, Equation (2.2). This model is used to design biological treatment system that utilizes a series of tanks to remove a pollutant. This model is applicable to wetlands because of their dead zones and short circuiting that are caused by the variation of plants, algae, and microbes along the flow path of the constructed treatment wetlands. Table 3 represents tracer studies of several wetlands

Table 3: Tracer Study of SSF CTWs

State or Country	Vegetation	Size (m²)	Depth (cm)	Tracer	Recovery (%)	nHRT (days)	Tracer HRT (days)	Volumetric Efficiency (%)	NTIS	Source
Quebec	*Phragmites*	1	25	Lithium	63	4.3	5.13	119	3.4	I
Quebec	Cattails	1	25	Lithium	65	5.95	4.54	76	2.5	1
Tennessee	Bulrush	5.9	45	Lithium	94	1.75	2.01	115	5.3	2
Tennessee	Bulrush	5.9	45	Lithium	100	1	0.83	83	6	2
Tennessee	Bulrush	5.9	45	Lithium	59	4.88	6.71	138	4.9	2
Tennessee	Bulrush	5.9	45	Lithium	160	1.61	1.67	103	5.6	2
Tennessee	Bulrush	11.8	45	Lithium	89	1.75	1.8	103	7.2	2
California	Cattails	15	95	Bromide	94	9.7	8.66	89	23.4	3
California	None	15	95	Bromide	99	9.7	11.13	115	24.1	3
Spain	*Phragmites*	55	50	Bromide	86	5.13	5.25	102	3.4	4
Spain	*Phragmites*	55	50	Bromide	106	5.13	5.17	101	3.4	4
Spain	*Phragmites*	55	50	Bromide	99	5.13	4.5	88	5.3	4
Spain	*Phragmites*	55	50	Bromide	92	5.13	7	137	8.3	4
Spain	*Phragmites*	55	50	Bromide	94	5.13	5.5	107	6.7	4
Spain	*Phragmites*	55	50	Bromide	105	5.13	6.54	128	11.1	4
North Carolina	Bulrush	61	60	Lithium	98	5.3	4.61	87	6.8	5
North Carolina	None	61	60	Lithium	96	2.9	2.58	89	7.2	5
New Zealand	-	132	78	RWT		4	2.55	64	4.5	6
New Zealand		132	78	RWT	-	4	3.6	90	5.5	6
Minnesota	Cattails	182	60	Bromide	84	15.1	12.1	80	4.8	7
Australia	Bulrush	400	69	RWT		4.23	4.02	95	13.8	8
Australia	Cattails	400	68	RWT		4.2	3.08	73	21	8
Australia	None	400	45	RWT	-	3.1	3.41	110	25.2	8
France	*Phragmites*	605	72	Chloride	96	3	2	67	10	9
France	*Phragmites*	605	72	Chloride	82	1.48	1.79	121	16	9
France	*Phragmites*	605	72	Chloride	87	4.34	3.29	76	14	9
France	*Phragmites*	605	72	Chloride	78	2.99	1.88	63	7	**9**
France	*Phragmites*	605	72	Chloride	91	1.28	1.29	101	11	9
France	*Phragmites*	605	72	Chloride	93	3.03	1.5	50	9	9

that suggest that the TIS Model is more reprehensive of the hydraulics of a wetland than the Plug Flow Model. (Kadlec and Wallace, 2009)

TIS Model

$$\left(\frac{C - C^*}{C_i - C^*}\right) = \left(1 + \frac{k\tau}{Nh}\right)^{-N} \quad \textbf{(2.2)}$$

Where:
k = first order removal constant , m/d
N = Number of Tanks in Series
h = Water depth, m
τ = Tracer detention time, d
C_i= Influent Concentration, mg/L
C = Effluent Concentration, mg/L
C*= Background Concentration, mg/L

Many pollutants that CTWs are designed to remove are mixtures or compounds of several elements such as biological oxygen demand, total suspended solids, and nitrogen. Some pollutant mixtures have light volatile materials that once exposed to the environment are stripped from the pollutant and are considered to be weathered. The P-K-C* Model utilizes a relaxed TIS Model equation to account for these pollutant mixtures and the reduction of pollutants due to weathering. P represents the TIS number and it is assumed its upper bound is N, or the number of TIS, develop during tracer studies. P can then be implemented into a relaxed TIS Model, Equations (2.3). The removal rate constant, k utilized in the equations accounts for pollutant lost due to weathering. In studying wetland performance P, k, and C* become dependent variables that can be adjusted to find estimates of each other. Implementing the P-K-C* Model allows for better data fitting through a statistical analysis of observed data. (Kadlec, 2003).

Relaxed TIS Model

$$\left(\frac{C - C^*}{C_i - C^*}\right) = \frac{1}{\left(1 + {}^{k}\!/\!_{Pq}\right)^{-P}} \quad \textbf{(2.3)}$$

Where:
k = first order removal rate constant , m/d
P = apparent number of TIS
q = Hydrualic Loading, m/d
C_i= Influent Concentration, mg/L
C = Effluent Concentration, mg/L
C*= Background Concentration, mg/L

D. Natural Media Filtration (NMF) Overview

NMF is a filtration process where wastewaters are percolated through some naturally occurring substrate or media. A typical cross section of a small NMF can be found in Figure (2.2), which also gives design loadings and removal characteristics. The natural media may consist of soils, compost, peat, manure, sand, or some other organic substance and is selected depending on the type of pollutant that will be removed. Pollutants such as metals, organics, nutrients, oil and grease, and total suspended solids (TSS) are trapped and adsorbed into the media. Natural media mechanically filters TSS and other micro-particulates from the wastewater as traditional filters do, but it also provides an organic media to adsorb soluble organics such as polychlorinated-biphenyls (PCBs). Ionic pollutants are removed through ionic exchange with the abundant exchangers, both anionic and cationic, in medias like compost and peat. Natural media also contains large amounts of organic carbon that can be utilized in simple oxidation/reduction reactions to remove pollutants such as residual chlorine. NMF also provides a biological substrate the microbial degradation

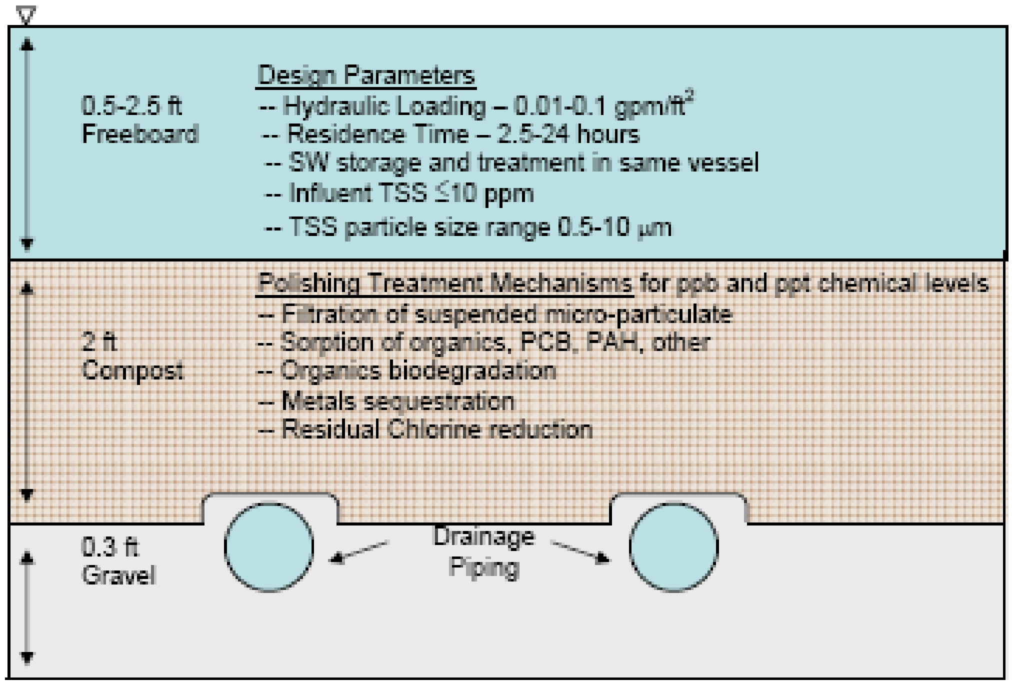


Figure (2.2) Natural Media Filter Cross Section

of organics. (Smith, 2005)

Currently NMFs are being used for metal removal because the amounts of humic substances found in compost or other decomposed organic matter. The metals are removed through electrostic bonding with the humic substances, cationic exchange, or chelation as the water percolates through the media. The humic substance in compost can also provide a large number of sorption sites that can capture oil and grease, nutrients and organics.(Smith, 2009) Humic substances are considered to have “Supramolecular Structures” and are a collection of small bio-organic molecules that are produced by the microbial degradation of plant and animal tissues. This “Supramolecular Structure” makes humic substances very stable and in most cases insoluble with a large molecular weight. Humic substances can consist of both humic acids, fulvic acids and humins. Humic and fulvic acids are humic substances that are insoluble in acids while humins are humic substances that are insoluble in bases. Humic substances can refer to a wide range of chemical compounds, but the dominate functional group in humic substance are phenolic and carboxylic groups.

Since natural media, in particular compost, can both filter and adsorb pollutants it has long been considered a potential media for PCB removal. Studies have shown that poly aromatic hydrocarbons (PAHs) and phenols can be removed from water by humic substances through adsorption and partitioning in the filter media due to their hydrophobic nature. Since PCBs are similar in structure and characteristics it is assumed that humic substances will remove PCBs in a similar fashion.(Clark and Pitt) Other studies performed by the University of Michigan and the Michigan Department of Environmental Quality showed that PCB degradation was accelerated when PCB contaminated soil was mixed with compost. (Michel Federick) The increased temperatures, microbial diversity, microbial activity and organic matter found in compost are assumed to stimulate the microbial degradation of synthetic compounds (California, 2002) such as PCBs.

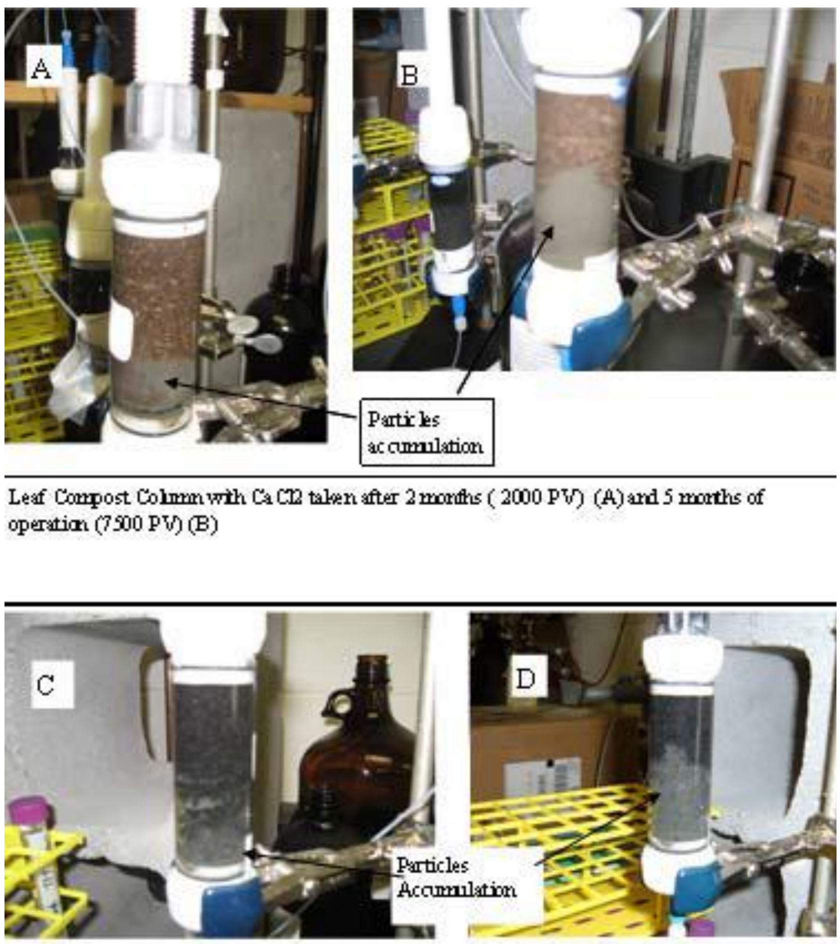
E. Alcoa Inc. Natural Media Filtration Research

Due to the use of PCBs in aluminum manufacturing and electrical transmission some of Alcoa Inc.'s industrial plant sites have low levels of PCB contamination in their storm and industrial wastewater discharges. Currently most sites in Alcoa use the standard best available technology (BAT) of a sand filter followed by granulated activated carbon (GAC) to remove PCB contamination, but this technology is becoming more expensive as discharge limits decrease and become more stringent. Alcoa Inc. has started to research new technologies that can remove low levels of PCBs from wastewater streams to meet the lower discharge limits at a reduced cost. The Alcoa EHS Technology Group located at the Alcoa Technology Center has performed multiple lab and field scale pilot studies to evaluate the potential of using NMF as treatment technology to remove low levels of PCBs from Alcoa wastewater discharges.

1. Alcoa Inc Lab Studies

One of Alcoa EHS Technology Group's major findings, in correlation with Clarkson University, was that due to PCBs hydrophobicity the majority of PCB contamination in water is due to the colloidal phase (ATC Report # 07-153). As discharge limits decrease, microfiltration will need to be added to the BAT to remove mircoparticulates. This was discovered during a lab test where low level PCB contaminated water was passed through four filter columns, two filled with leaf compost and two with granulated activated carbon (GAC). To better understand the particle movement in the fixed bed filters the influent water from one column of each media was fed $CaCl_2$ along with the PCB contaminated water. These columns were operated with an empty bed contact time (EBCT) of 50 min at a hydraulic loading of 0.04 gpm/ft^2 for 6 months. The experiment indicated that the NMF performed similarly to GAC as the particles moved through the filter bed as shown in Figure (2.3). Both media allowed some particles in the size range 0.01 – 1μm to pass through the columns. These particles had little effect on the total mass of PCBs and there were no detectable PCBs in the effluent. (ATC Report # 07-153)

After the initial column test indicated that NMF PCB removal was comparable to GAC, the Alcoa EHS Technology Group developed a more robust bench scale pilot. This pilot was used to test the technology on PCB contaminated wastewaters from two of its industrial facilities. The bench scale pilots consisted of a five gallon rectangular glass aquariums filled with compost of varying types, depending on the experiment.



Leaf Compost Column with $CaCl_2$ taken after 2 months (2000 PV) (A) and 5 months of operation (7500 PV) (B)

GAC Column with $CaCl_2$ after 2 months (2000 PV) (C) and after 5 months of operation (7500 PV) (D)

Figure (2.3) Particle Movement in NMF Columns

For all experiments an under drain of pea gravel and sand was placed on the bottom of the tanks. Compost was then placed on top of the under drain. Two pumps and distribution headers were set up in the tank using teflon hose and adjustable centrifugal pumps. One header was placed under the gravel/sand under drain and the other on top of the mulch. Then influent wastewater was fed to the top of the tank and free board was allowed to develop. This head pressure would create a downward flow through the compost. The effluent would then be removed by the header at the bottom of the tank. The influent pump would be set at the designed flow rate, depending on the desired hydraulic retention time (HRT), and the effluent pump was adjusted to get the proper suction to match the designed flow rate. Figures (2.4) show the steps take to build the bench scale pilot NMFs. (ATC Report # 05-049)

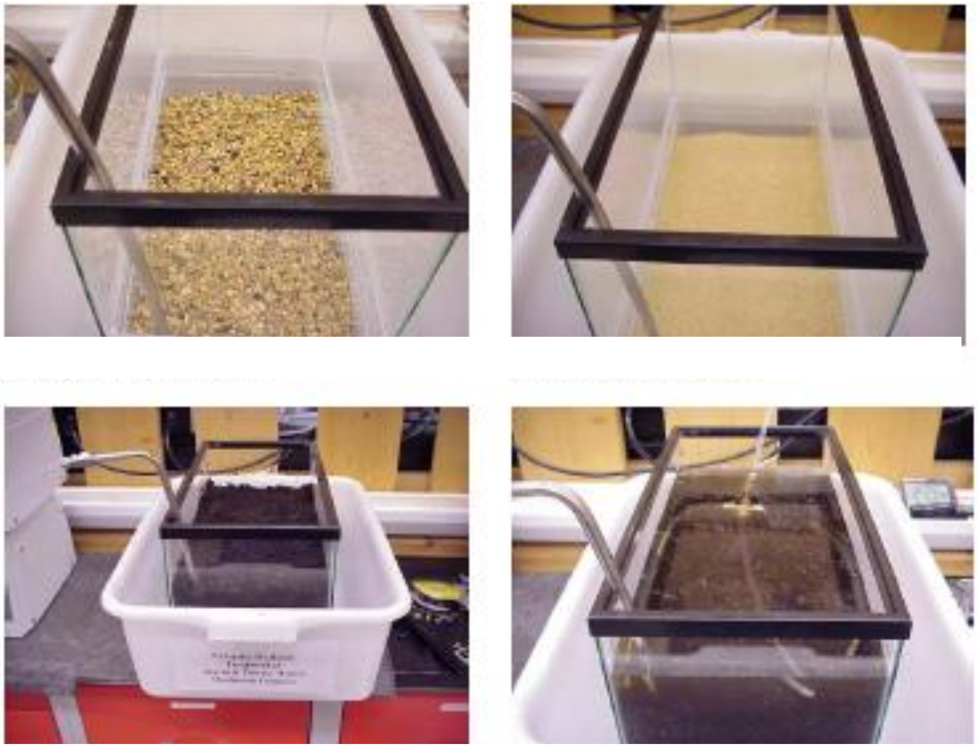


Figure (2.4) NMF Bench Scale Pilot

2. ALO Bench Scale and Full Scale Pilots

The EHS Technology Group first tested PCB contaminated wastewater from Alcoa ALO facility. Treated wastewater from the facility was being discharged into an existing sewer system and as it traveled through the sewer system to the plants outfall it would become contaminated with PCBs. The sewer system was a combined system and storm water was also becoming contaminated with PCBs. To meet upcoming NPDES permit limits, the facility was proposing to install an 8 million dollar sandfilter and activated carbon wastewater treatment plant at its outfall. This system would remove the PCB contamination from both its dry-weather (DWF) and wet- weather (WWF) flows. The EHS Technology Group proposed to perform a treatability study on the ALO wastewater to determine if a NMF would be a low cost treatment option for removing the PCBs.

Samples of both WWF and DWF were sent to the EHS Technology Group for bench scale testing. The wastewater was passed through the five gallon aquarium bench scale systems that the EHS Technology Group had developed. A conceptual design of a full scale system indicated that one million gallons of water would need to be treated per day and would require two million gallons of compost with a two day hydraulic retention time. Scaling this down, the bench scale pilot was built with 3.3 gallons or about 2 ft of compost and 1.65 or about 1 ft of freeboard with a pea gravel and sand under drain. The wastewater was fed into the system at 4.3 ml/min and the water was pushed vertically through the compost by head pressure. For DWF two different types of compost were utilized, standard mushroom compost and a locally available mushroom compost (Green Grow) with all other variables being kept constant in both systems. Both systems where first flushed with DI water for three days and on the fourth day the DWF wastewater was fed into the system. The DWF was then passed through both systems for ten days. The influent concentration of total PCBs in the DWF was about seventy parts per trillion. The effluent water was sampled for total PCBs on days two, six, and ten with all results being below the detection limit of six parts per trillion of the utilized conger analysis (motified Green Bay Method) for both types of mushroom compost. Figure (2.5) shows the results of the DWF sampling.

As the initial testing of the DWF indicated both compost removed PCBs down to non-detectable levels even though their total organic carbon content varied by 13%, 14% for Green Grow and 27% for standard mushroom compost. Due to this fact only the Green Grow compost was used to treat the WWF from ALO. The flow into the aquarium containing Green Grow compost was switched to the WWF from ALO on day fifteen. The system was run for thirteen days at a HRT of two days and than lowered to a HRT of half a day for an additional five days. The WWF had an influent concentration of total PCBs of 2,120 parts per trillion and the effluent was sample on days thirty three and thirty five of total operation. Both samples returned a result of non-detect for total PCBs. Figure (2.6) is a summary of the all samples performed on the Green Grow Pilot unit. (ATC Report # 05-049)

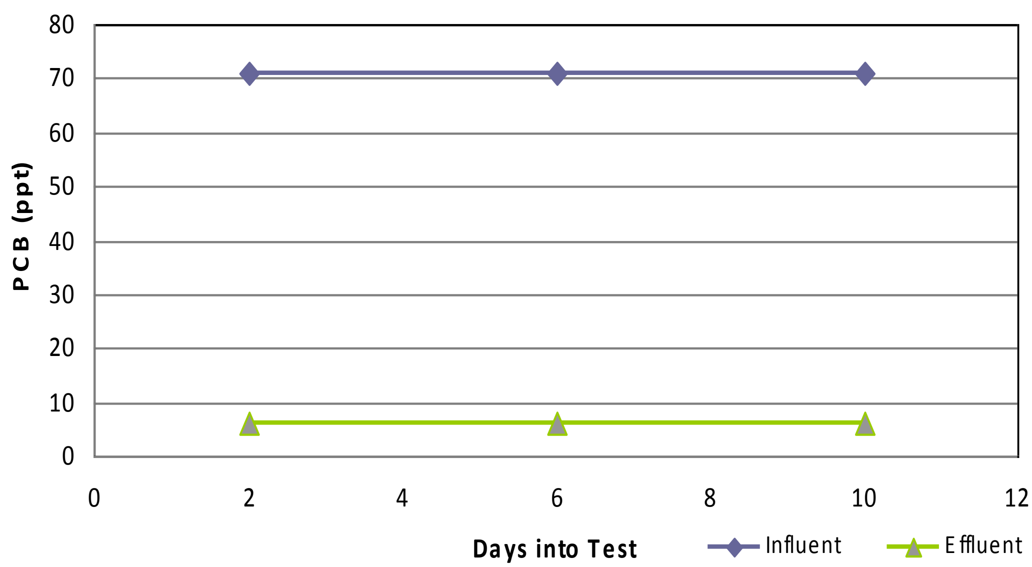


Figure (2.5) Dry Weather Flow Mushroom NMF PCBs Results

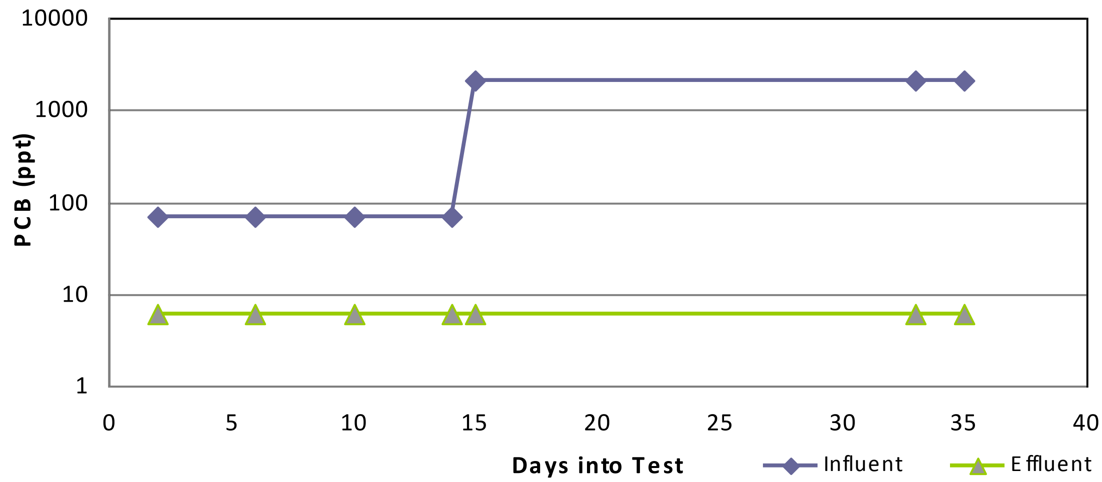


Figure (2.6) Dry Weather Flow Green Grow NMF PCBs Results

After other successful bench scale testing of PCB contaminated wastewater the EHS Technology Group developed and built a full scale pilot unit at ALO. This unit was designed to handle all of the ALO DWF and the first flush of its WWF. The system consisted of one foot gravel under drain, two feet of leaf compost, and piping similar to the bench scale design. Leaf compost was chosen for the full scale pilot NMF because due to the large volume needed it was the only compost available locally. Other bench scale pilot NMF studies performed by the EHS Technology Group showed that the leaf compost had the same PCB removal properties as the mushroom compost. The full scale pilot flow rate varied from thirty two gallons per minute (gpm) to 258 gpm. The unit was capable of treating 100,000 gallons (DWF) to 350,000 gallons (WWF) of PCB contaminated wastewater a day with HRT varying from 4 – 17 hours. The hydraulic loading rates varied from 0.019 to 0.08 gpm/ft^2. Figure (2.7) through (2.9) consist of picture taken during construction of the field scale pilot.

Figure (2.7) – ALO NMF Cell Piping and Gravel Under Drain

Figure (2.8) – ALO NMF Cell Compost Being Applied

Figure (2.9) – ALO NMF Cell in Operation

Pumps were placed in an existing combined sewer manhole to pump water into the NMF. As mentioned earlier the NMF was designed to handle all of the DWF from ALO, but during storm events float switches were used to keep the NMF cell freeboard full. Once the NMF was filled, the pumps would shut off and the storm water would be allowed to bypass the NMF. After nearly a year of operation the unit was able to constantly achieve effluent PCB concentrations of less than one hundred parts per trillion, which was below the detection limit of the permit analytical method, Aroclor Method 608. Also two effluent samples were collected and analyzed using the Modified Green Bay method with results of non-detect as represented in Figure (2.10).

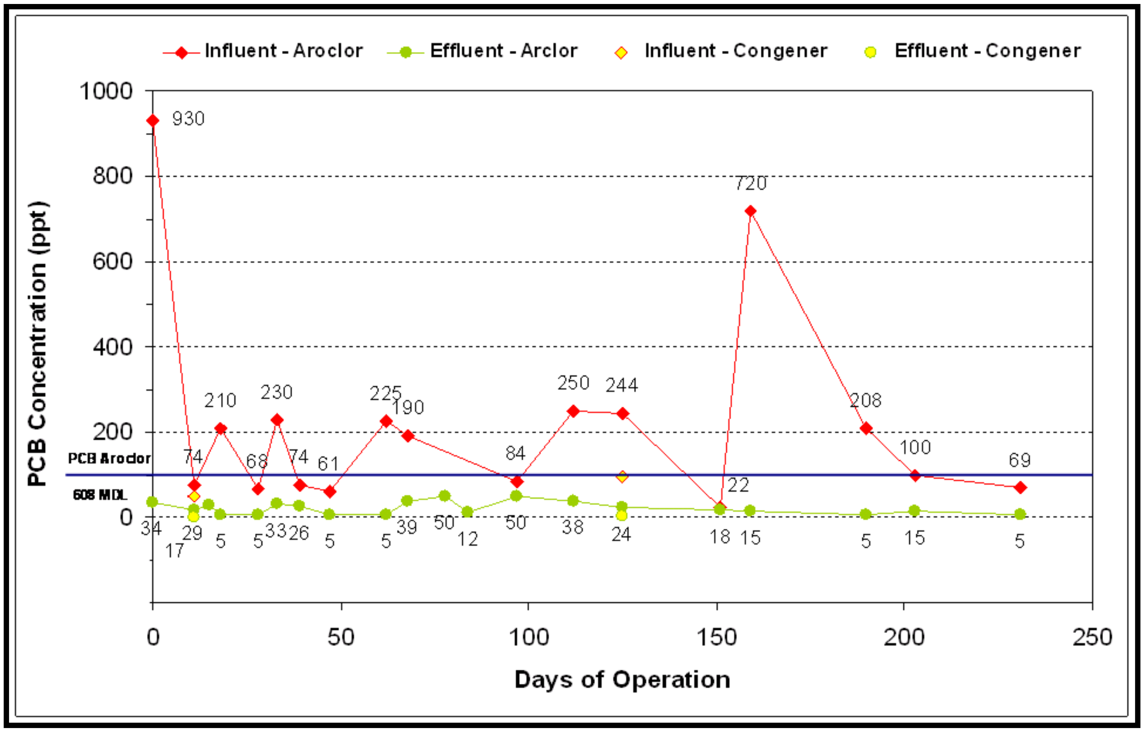


Figure (2.10) ALO Full Scale Pilot PCB Results

The field scale pilot NMF was installed at a cost of less than a hundred thousand dollars compared to the proposed cost of $8 million for a sand and activated carbon filter system. At the time of start up of the NMF, ALO was operating a filter bag treatment system to treat all of its dry weather flow. After the first year of operation ALO modified its NPDES permit to shut down its bag filter system and in place used the NMF for final treatment of DWF. This immediately gave ALO an annual operation and maintenance cost of $60,000 per year since the NMF requires relatively little maintenance. (Smith, 2005)

During operation of the full scale pilot it was observed that the compost was beginning to settle and cracks started to appear on the surface of the media. These cracks were racked smooth and there was no lost of treatment efficiency. Also during the summer of the first year of operation an algae bloom appeared on the surface of the compost. A sonic algae killing devise was installed to try and control the algae, but the devise had little affect on the system. After the algae bloom occurred it was noticed that the hydraulic conductivity of the system was decreasing. It had gone from 0.0094 cm/sec to 0.0006 cm/sec which reduced the NMFs capability to treat the first flush of WWF. A study was performed by the Alcoa EHS Technology Group to determine the cause of the reduction in hydraulic conductivity. This study revealed that the combination of bio-fouling from the algae, TSS loading during storm events, and media consolidation were all contributing to the reduction in hydraulic conductivity. Conclusions from the report suggested that in future pilot studies measures should be taken to control algae blooms in NMFs and that life spans of NMFs will be shortened if they receive high concentrations of TSS. (ATC Report # 06-060).

3. ME Bench and Full Scale Pilots

Alcoa ME Plant had similar legacy issues with PCBs in their combined sewer system. Their sanitary wastewater was becoming contaminated with low level PCBs as the wastewater moved through the combined storms. The sanitary water was being treated through a typical biological wastewater treatment facility, but ME had to operate a dual media rapid sand filter and activated carbon filter as a polishing unit to remove PCBs down to non-detectable levels before discharge. This best available technology (BAT) was achieving its goal of removing PCBs from ME's effluent stream, but still experienced periodic failures that resulted in NPDES permit violations. After the success of the ALO bench scale pilot the EHS Technology Group proposed to test the ME sanitary wastewater to see if a NMF would be a low cost option for replacement of the current BAT that would consistently meet effluent limits. (ATC Report # 08-0110)

For the bench scale NMF pilot, seven 55 gallon drums of treated sanitary wastewater, pre activated carbon unit, were shipped to the EHS Technology Group's lab. Utilizing the same aquarium bench scale pilot and same unchanged media that was used in the ALO pilot, the EHS Technology Group started treating ME sanitary wastewater. Only the aquarium filled with mushroom compost was used in the ME pilot since during the ALO pilot there was no observed difference between the two composts. The ME pilot was initially ran with the same HRT, 2 days, as the ALO pilot of two days, but was reduced down to 0.031 days has the pilot progressed. This subsequently made the HLR increase from 0.001 gpm/ft^2 to 0.09 gpm/ft^2. This was done to test the robustness of the NMF and to attempt to find the breakthrough point of the system. The sanitary wastewater that was shipped to the EHS Technology Group had PCB influent concentration varying from 94 to 1,304 parts per trillion, measured using the Modified Green Bay method. As Figure (2.11) shows all of the effluent samples had non-detectable PCB concentrations similar to the ALO pilot. The EHS Technology Group was impressed by the NMF's ability to filter the increased PCB loading and the pilot was completed before the breakthrough could be determined. (ATC Report # 05-055)

During the ALO bench scale pilot it was observed that for the first few days of operation the NMF effluent was heavily colored, but reduced each day of operation, see Figure (2.11). Due to this coloration during the ME bench scale pilots extra sampling was performed on the NMF effluent to determine what affects it was having on the wastewater other than PCB removal. The color was assumed to be caused by organic matter being released from the mushroom compost. Total organic samples were taken throughout both the ALO and ME bench scale pilots. During initial start up the total organic carbon (TOC) was above 200 mg/l, but decreased throughout the thirty days of operation with a final value less than 10 mg/l of TOC. This reduction in TOC corresponds with the reduction in color of the effluent from 20,000 PCUs to 0 PCUs over the thirty day period. The EHS Technology Group concluded that until the media consolidates and becomes fully saturated some of the organics of the compost will be released, but this coloration will only last for the first few days of startup.

The effluent was also sampled for total suspended solids (TSS), total nitrogen (TKN), C-BOD5, oil and grease, dissolved oxygen and eH. Results of TSS sample, though varied, indicated that the TSS would be higher than the influent during the first few days of start up, but should reduce as the system was operated. For total nitrogen the ME NMF effluent levels were much higher than that of the influent. The EHS Technology Group proposed that the NMF was causing the increased nitrogen levels, but that further large scale pilots would need to be performed.

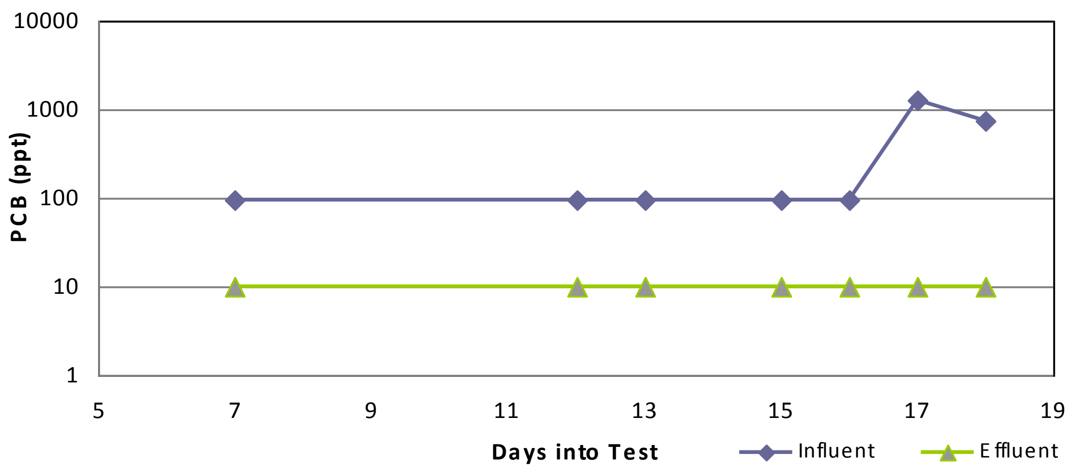


Figure (2.11) ME Mushroom NMF PCBs Results

Figure (2.12) Color samples During NMF Start Up

The NMF had no affect on either C-BOD5 or oil and grease, Influent concentration matched effluent concentrations for both parameters. As predicted, due to anoxic zones in the NMF, both the DO and eH of the effluent water were much lower than that of the influent with the lowest levels being 1.6 mg/l DO and -44 eH. Again here the EHS Technology Group suggests that this issue should be further studied in a larger scale pilot.

After the initial success of both the ALO bench and full scale pilots as well as the success of the ME bench scale pilot a field scale NMF pilot was set up at ME. A sixty four inch diameter tank with a conical bottom was filled with twenty four inches of mushroom compost and gravel under drain. Figure (2.13) provides a schematic of how the NMF was set up and operated. Influent from the sanitary wastewater system was pumped into the top of the tank at two gallons a minute, giving the system a hydraulic loading of 0.1 gpm/ft^2. After flushing potable water through the system for six days to allow for the color to be flushed, sanitary water was fed into the NMF. For the first three days of operation the NMF effluent was non-detectable for PCBs, but on the eighth day of operation PCBs were detected in the effluent. On the fifteenth day of operation the NMF experienced complete breakthrough and was having no affect on PCB removal, see Figure (2.14). Original assumptions were that the system was short circuiting because a seepage collar installed around the sidewall of the tank had come loose and the compost may have consolidated. To test this theory a dye test was performed on the system which concluded that short circuiting did not occur. (ATC Report # 08-110)

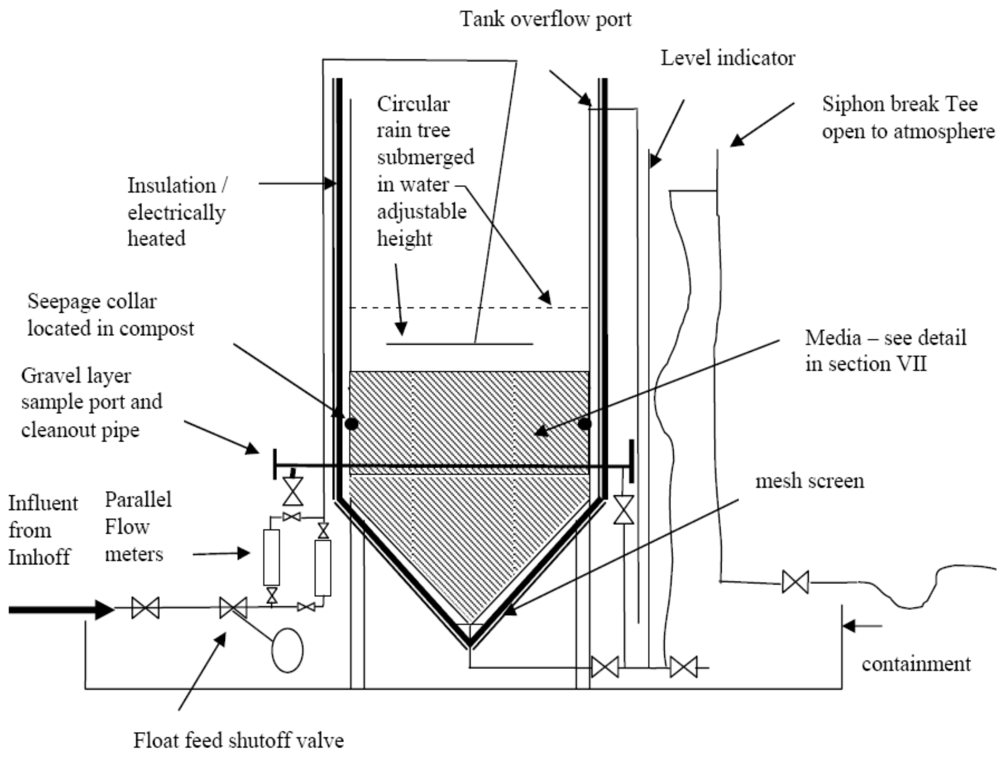


Figure (2.13) ME Full Field Pilot Cross Section

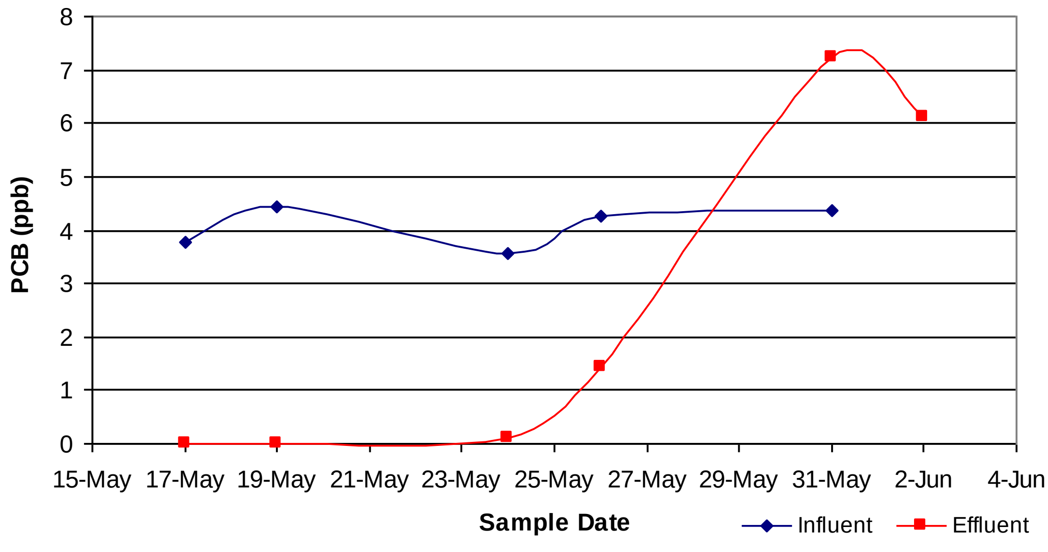


Figure (2.14) ME Mushroom NMF Field Pilot PCB Results

Previous studies done by the Alcoa ME plant had determined that past failure of the sandfilter and carbon filters was due to PCBs that had absorbed to sub-micron sized organic particulates from the facilities activated sludge process. After the failure of the mushroom compost it was removed and replaced with leaf compost used at the ALO full scale NMF. The leaf compost had a small grain size distribution curve and should intern been more effective at removing small particulates. After the leaf compost was flushed with potable water the sanitary effluent was routed into the NMF at a half the loading rate of the mushroom compost, 0.05 gpm/ft^2. The leaf compost NMF had mixed results with PCBs appearing in the effluent initially, then being non-detect, and finally completely breaking through.

It is assumed that the failure of the leaf compost NMF was also due to the sub-micron sized particulates that contain PCBs. The EHS Technology Group theorized that since the PCBs had already absorbed to the colloid particles they would have less affinity to absorb to the compost and were allowed to pass through the bed. This characteristic of the ME sanitary wastewater was not discovered in the lab scale pilot because the samples sent to the lab were "aged" for two weeks and coagulation of the sub-micron particles most likely occurred. The EHS Technology is currently still doing research into the removal of micro-particulates by NMFs. (ATC Report # 08-011)

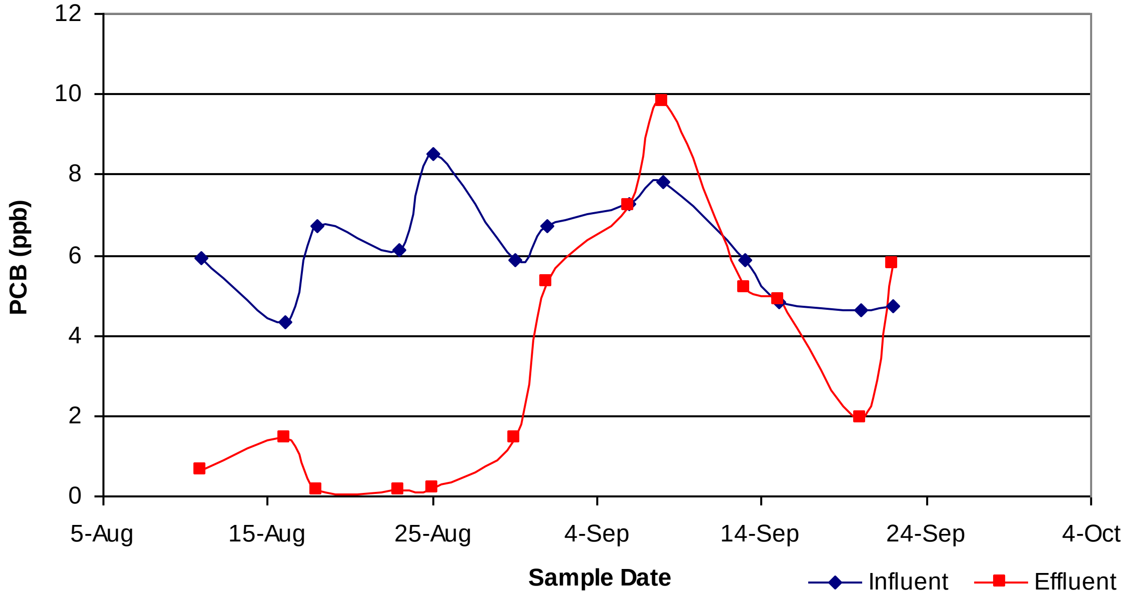


Figure (2.15) ME Leaf Compost Field Pilot PCB Results

CHAPTER III
MATERIALS AND METHODS

A. Site Description

Alcoa Inc. North Plant Outfall 007 currently captures and treats landfill leachate for the North Plant Landfill. This landfill is located on the north end of the of Alcoa Tennessee Operation's (TN Ops) North Plant. The landfill was used to dispose of construction debris, scrap metal, earthen material and other industrial waste starting in 1944. At many different times in the past Alcoa Inc. used the site as liquid waste impoundments. The North Plant primarily operates aluminum rolling mills and the rolling emulsions from these mills were discharged into the impoundments for treatment. The emulsion was treated by adding aluminum sulfate and organic polymers to break the oil emulsion. The oily alum sludge settled to the bottom of the lagoons and the water was discharged. In 1976, Alcoa Tennessee Operations (TN Ops) installed a wastewater treatment facility that replaced the impoundments. Hydraulic oils from the rolling mills were also discharged for treatment into the impoundments and were assumed to contain high levels of PCBs

In the 1960s, TN Ops discovered an oily water seep coming from the northwest toe of the landfill and placed a dike around the seep to create a leachate containment pond. An underflow type weir was placed in the pond and the water was allowed to discharge through the baffle that prevented free phase oil from leaving the pond. The last series of impoundments located on the North Plant Landfill were closed in the

1980s and a clay cap was placed over the filled in impoundments. The seepage pond was modified to better capture the floating oil coming form the landfill with the leachate and an oil skimmer was installed to help remove the free phase oil from the pond. This leachate discharge point was permitted as Outfall 007 (Geraghty & Miller Report, 1981)

In the late 1980s a renewed NPDES permit required TN Ops to install a wastewater treatment system at Outfall 007 to remove PCBs, oil and grease, and ammonia from the discharge. The system consisted of a trickling filter for oil and grease removal, attached growth nitrification, pressure filters, and activated carbon for PCB removal. In 2007 it became evident that the current mechanical treatment system was coming to the end of its life and a replacement was needed.

The goal for the replacement was to find a low cost low maintenance system that would ensure compliance. Since Alcoa Inc. had varying success with PCB removal using NMF at other locations, it was determined that this was another potential arena to test this technology. It was assumed that the NMF would be able to remove the PCBs from the leachate and accomplish the goals of being both low cost and low maintenance. After start up of the NMF pilot unit it was determined that the NMF would not be able to remove the ammonia form the leachate. It was decided that if TN Ops was going to go to a full scale system with a NMF the best scenario to treat the ammonia and other contaminates of concern would be to install a CTW. By using a CTW,TN Ops hope to demonstrate that an Engineered Natural System (ENS), the wetland plus the NMF, could remove all contaminates of concern from the leachate. The ENS would also be a low cost, long term solution to this legacy issue. In March of

2007 Alcoa EHS Technology Group supported the installation of a pilot NMF and later a subsurface wetland at Outfall 007.

B. Pilot Natural Media Filter (NMF)

The first step in building a pilot NMF was to determine what type of natural media would be used and what type of container the media would be placed in. From data obtained at pilot units operated at Alcoa ME and ALO it was recommended, by the Alcoa EHS Technology Group, that mushroom compost be used as a filter media for the Outfall 007 pilot. The next step was to determine what type of container would be utilized to hold the media. From the potential short circuiting that occurred at other pilot NMF, it was determined that a ridged tank would need to be used for the Outfall 007 pilot and that an up-flow system would be the most effective way to eliminate short circuiting. An 830 gallon stainless steel tank that had been designed for other purposes was found and modified to use as the NMF container. The dimension for the 830 gallon tank can be found in Figure (3.1).

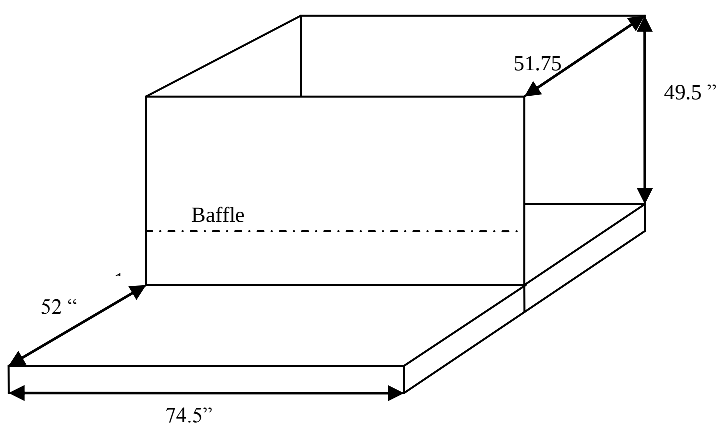
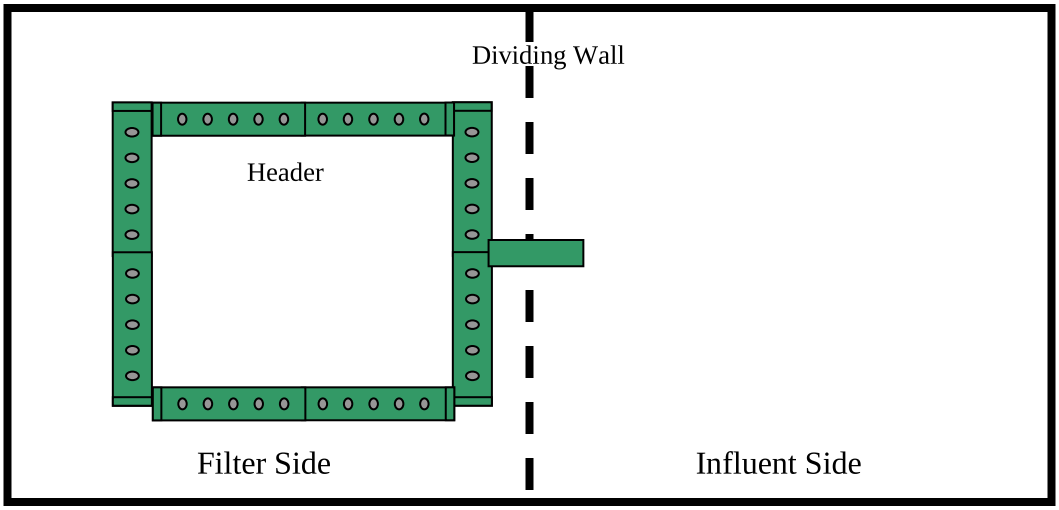


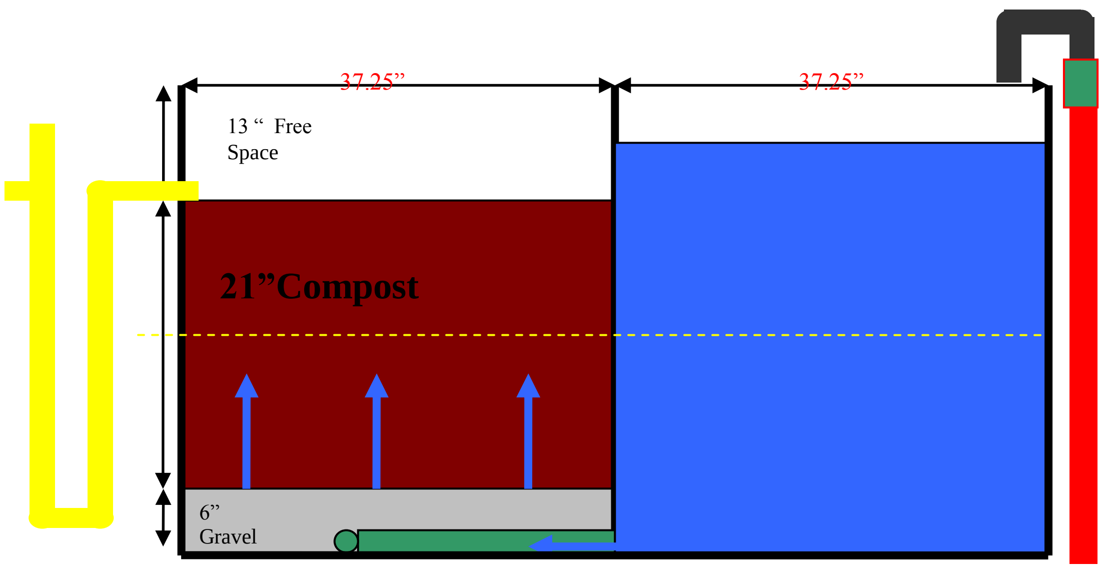
Figure (3.1) TN NMF Box Dimensions

The goal in building the NMF was to operate the system with the least amount of mechanical influence as possible. To accomplish an up-flow filter it was determined that the box would be divided into two sections. The water elevation on the right side, influent side, of the box would be set at a certain height using a standpipe on the outside of the box, see Figure (3.2). An under drain was placed through the dividing wall and a distribution header was installed on the left side, filter side, of the box as shown in Figure (3.2). The standpipe on the filter side of the box, see Figure (3.3), would be set lower than the influent side of the box. The equalization of head between the two sides of the box would create the up pressure needed to drive the leachate through the mushroom compost. The heads on both sides of the unit would be adjusted until the desired flow rate was achieved.

Once the tank was modified and the flow patterns were determined the media placement was then determined. It was determined that six inches of 1 to 1.25" gravel would be placed over the distribution header on the filter side of the box. To enhance the absorption capabilities of the mushroom compost it was recommended, by the Alcoa EHS Technology Group' to mix the mushroom compost with granulated activated carbon on a dry weight one to one ratio. The mushroom composted that was used had a moist density of about 52 pounds per cubic foot, or about 7 pounds per gallon, and the granulated activated dry carbon weighed about 28 pounds per cubic foot, about 3½ pounds per gallon. To obtain the desired ratio the filter media was placed in the tank in lifts. Two 5 gallon buckets of mushroom compost would be placed on top of the rock and then one 5 gallon bucket of activated carbon. The two materials were then mixed



Plan



Cross Section

Figure (3.2) TN NMF Plan and Cross Section View

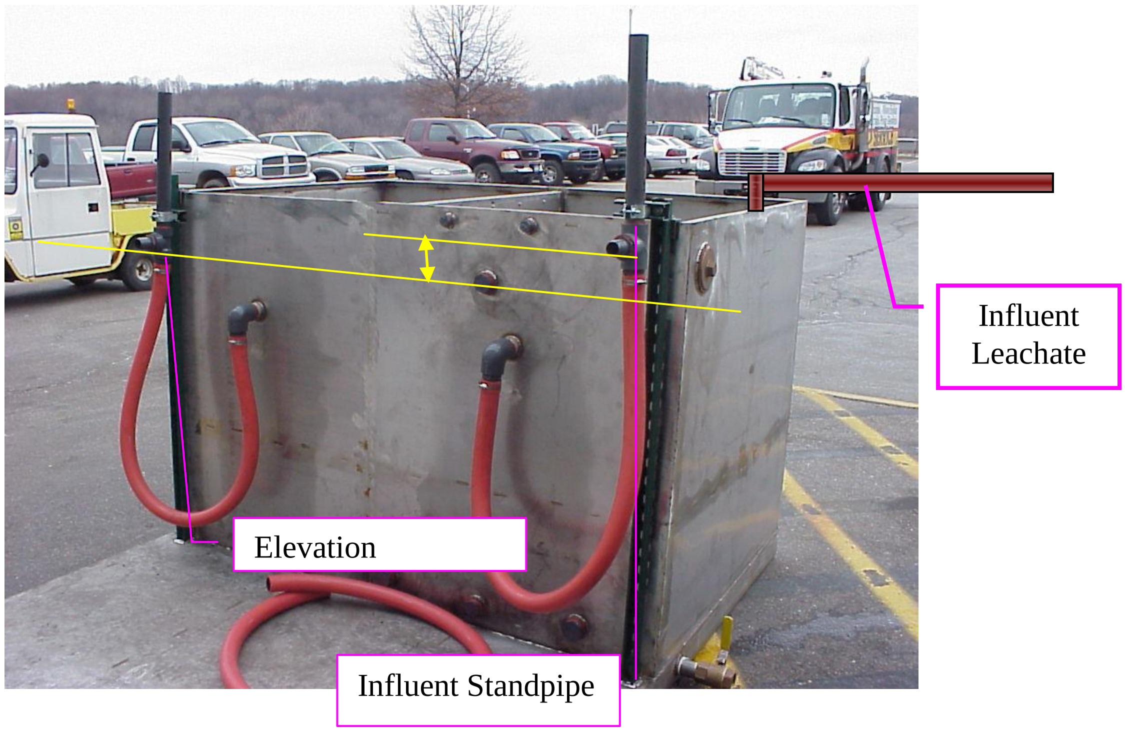


Figure (3.3) TN NMF Picture

by hand, tapped, and another lift was added. This step was repeated making sure to keep the 2:1 ratio until the desired depth of twenty one inches was reached. This gave an empty bed volume of twenty four and a half cubic feet.

Hydraulic conductivities, K_s, which covered the range of observed hydraulic conductivities from the ALO NMF pilots, were used to determine the flow rate through the Tennessee 007 NMF pilot. Due to the dimensions of the box utilized for the NMF the maximum headloss across the unit was thirteen inches. Historical max PCB and total suspended solid (TSS) data from the landfill leachate was reviewed to determine a loading rate. Table 4 shows the range of flow and loading rates.

Table 4: Flow Rate Determinations for TN NMF

dh (inch)	**13**	**dL (inch)**	**21**		**Inf PCB (ppt)**	**8000**
Area (SF)	**13.4**	**EB (gal)**	**175.41**		**Inf TSS (ppm)**	**10**
Ks (cm/s)	v (cm/s)	q (gpm/sf)	Q (gpm)	EBCT (minutes)	PCB Loading mg/day/sf	TSS Loading mg/day/sf
0.001	0.0006	0.0091	0.1222	1436	0.40	497
0.003	0.0019	0.0274	0.3665	479	1.19	1491
0.005	0.0031	0.0456	0.6108	287	1.99	2485
0.01	0.0062	0.0912	1.2217	144	3.98	4969
0.015	0.0093	0.1368	1.8325	96	5.96	7454
0.02	0.0124	0.1823	2.4434	72	7.95	9938

dh = headloss available across bed (13 inches maximum available)
dL = depth of compost in cell
v = Velocity (cm/s)
q = gpm/sf
Q = Flow (gpm)
EB = Empty Bed Volume (Gallons)
EBCT = Empty Bed Contact Time
C_{in} = Influent Concentration

It was recommended by the Alcoa EHS Technology group that the applied PCB loading rate be kept in the same range as the ALO pilots, 0.16 to 0.23 mg/day/ft^2**.** Using the range of flow rates calculated in Table 4, Table 5 was developed to determine what the different PCB Loadings would be in the TN NMF pilot at different observed PCB concentrations.

Table 5: PCB Loading Rates

	TN Min PCB	TN Avg PCB	TN Max PCB
Influent PCB (ppt)	200	2510	8780
PCB Loading (mg/day/sf) @ 0.2 GPM	0.016	0.204	0.714
PCB Loading (mg/day/sf) @ 0.4 GPM	0.033	0.408	1.428
PCB Loading (mg/day/sf) @ 0.6 GPM	0.049	0.613	2.143

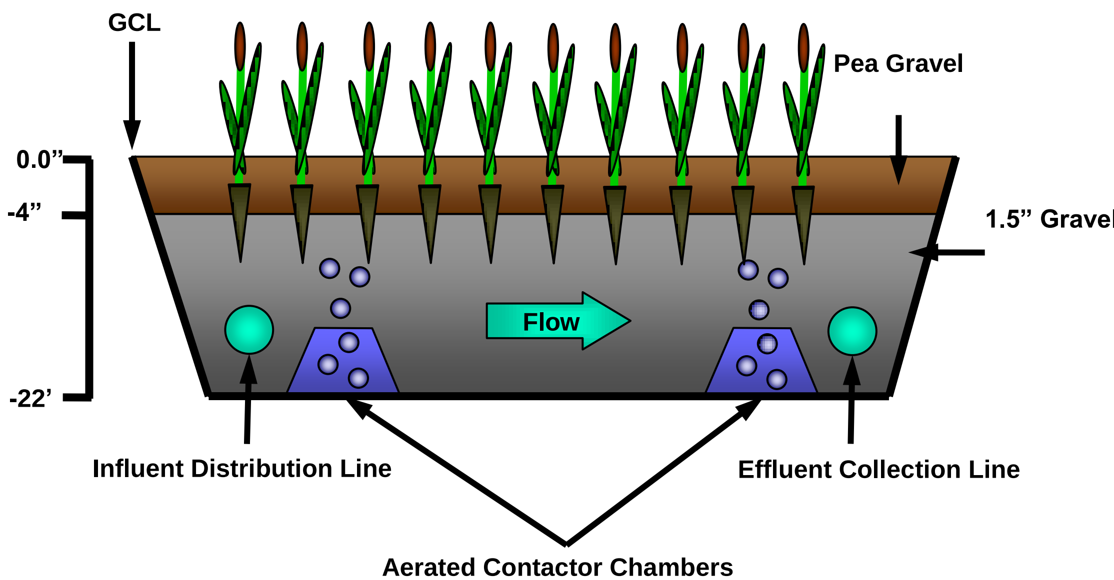
A flow rate of 0.2 gallons per minute (gpm) or about 750 ml/min was chosen for the TN NMF pilot to stay within the recommended PCB loading rate. After start up it was discovered that the designed method to utilize the influent standpipe to control the flow was not efficient and the designed flow rate could not be achieved. After two months of operation a metering pump was installed to better control the influent into the NMF. Leachate was pumped into the influent side of the NMF and the standpipe was set to not allow for overflow, causing all influent water to be pushed through the media. Effluent from the system was discharged back into the Outfall 007 leachate pond.

C. Constructed Treatment Wetland

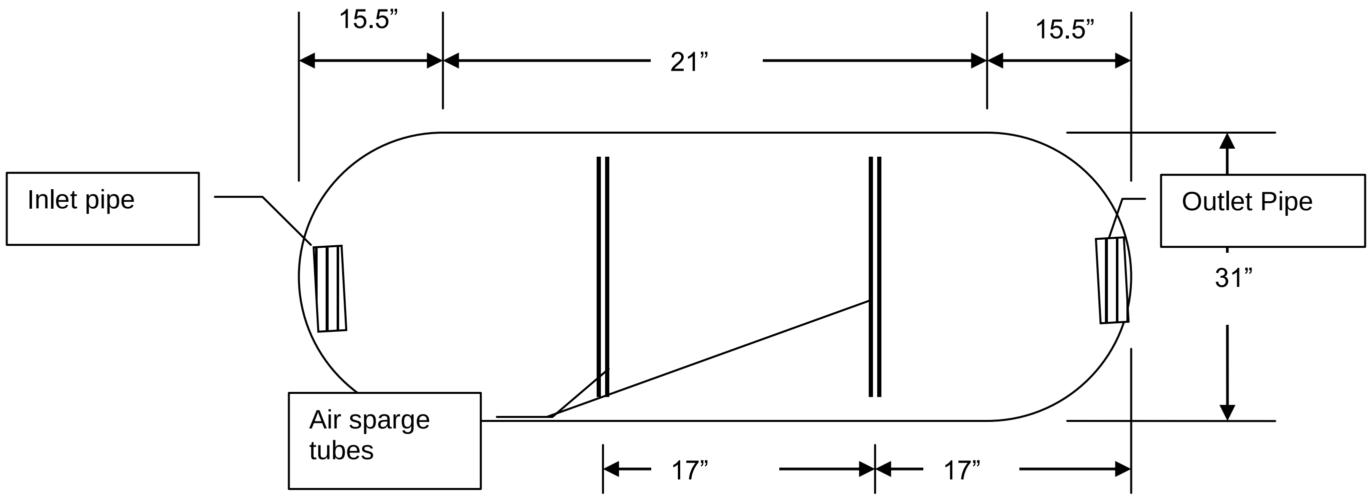
In May of 2007, after two months of operating the TN NMF pilot, a subsurface CTW pilot was installed in parallel to the NMF to attempt to remove ammonia from the leachate. A 300 gallon standard horse trough was filled with eighteen inches of 1 ½ inch gravel and four inches of ¼ inch pea gravel on top of the larger gravel. Once filled, the trough was assumed to have a void space equal to 100 gallons. Ten cattails were then removed from a local pond and were evenly planted across the surface of the constructed wetland. A plan and a cross sectional view of the CTW is show in Figure (3.5).

The goal of the larger gravel was to provide an area for microbial growth which would nitrify the ammonia. Air sparge tubes were placed at the bottom of the trough to create an aerobic system, but were never used. The cattails were placed in the pea gravel to uptake the nutrients that were being released by the microbial action in the lower levels of the wetland. The roots of the cattails also help to transfer oxygen into the system helping to promote an aerobic system. (Hammer, 1989) A metering pump was used to set the flow rate at 0.3 gpm, which gave the system a 2.2 day hydraulic retention time (HRT). Effluent from the system was discharged back into the Outfall 007 leachate pond.

Figure (3.4) TN CTW Picture



Cross Section



Plan

Figure (3.5) TN CTW Cross Section and Plan View

D. Sampling and Operation

The set up, sampling, and operation was performed by TN Ops employee, Clint Swires, with assistance from other Alcoa Inc. employees. After the initial set up, the NMF was started on 3/21/2007 and operation was stopped after the final sample on March 31, 2008. Since the NMF was an up-flow system, the NMF was operated at 300 ml/min for the first twenty four hours to allow the compost to stabilize. After the first twenty four hours the flow rate was increased to 950 ml/min. This initial flow rate was chosen to help to accelerate the color that is released from the initial start up of NMFs. The first samples were taken on 3/29/2007. The CTW was started on 5/3/2007 and allowed to run for ten days before being sampled. The CTW was stopped on January 15, 2008. The metering pump to control the influent to the NMF was installed in July of 2007.

Both the NMF and CTW were sampled weekly for the first four months of the study, two months for the CTW. The sampling was then spaced out to once a month during the last five months of operation. Table 6 is the sampling plan that was proposed by the Alcoa EHS Technology Group. Field meters, calibrated by TN Ops personnel, were used to take field readings for temperature, pH, dissolved oxygen (DO), oxidation reduction potential (ORP), and conductivity (Cond). Flow rates were measured with a stop watch and graduated cylinder and head differences between the two sides were determined visually with rulers. All other samples were analyzed by contract laboratory Microbac Inc. Knoxville Branch. Samples were collected in bottles provided by Microbac and EPA approved methods were used to analyze the samples.

Table 6: Outfall Pilot Sampling Plan

Parameter	Influent	Effluent NMF	Effluent CW
Ammonia (NH_3)	X	X	X
Nitrate/ Nitrate (NO_3/NO_2)	X	X	X
Phosphate (P)	X	X	X
Chemical Oxygen Demand (COD)	X	X	
Oil and Grease (O&G)	X	X	X
PCB	X	X	X
Alkalinity	X	X	
Total Suspended Solids (TSS)	X	X	X
Volatile Suspended Solids (VSS) **(NMF Only)**	X	X	
Dissolved Oxygen (DO)	X	X	X
Conductivity (Cond)	X	X	
Redox Potential (ORP)	X	X	
pH	X	X	X
Temperature (T)	X	X	X
Flow	X	X	X

After the initial start up there were very few modification made to either the NMF or the CTW. On July 6, 2007 locally available phosphate fertilizer was added to the CTW in an attempt to increase microbial growth in the wetland. As noted earlier the only other adjustments that were made to the system were adjustments in standpipes to reach the designed flow rate of the NMF and the installation of the metering pump.

The line that feeds leachate from the collection pond to the current treatment system was tapped to provide influent to the NMF and CTW. The water was fed into a fifty five gallon drum that was used as a surge tank. The metering pumps were then used to feed leachate into the NMF and the CTW. Field notes were taken during each sampling event to track ambient weather, appearance of influent and effluent water, and the condition of the leachate collection pond. Since 12% sodium hypochloride is used to control algae blooms in the leachate collection pond, notes were taken on when the hypochloride was being fed into the pond.

CHAPTER IV
RESULTS AND DISCUSSION

A. Constructed Treatment Wetland Sampling Results

The CTW was installed at Outfall 007 to test its ability to remove the ammonia from the landfill leachate. Though this was the primary focus of the study, other parameters were monitored to determine what affects, if any, the wetland had on these parameters. The results of these other parameters will be presented and discussed first. Next ammonia and nitrate/nitrite results will be presented and modeling equations presented in the literary review will be applied to the results to determine the accuracy of the models.

1. Total Suspended Solids (TSS)

As Figure (4.1) shows, the CTW was capable of removing TSS. The TSS in leachate at Outfall 007 is usually due to algae blooms in the collection pond. This is indicated by the extreme peaks in the TSS influent concentrations and the amount of volatile suspended solids (VSS) in the influent. The average effluent TSS concentration was 9.4 mg/l, with a max of 36.0 mg/l. Suspended matter is removed in the wetland through filtration. As the water passed through the media of the wetland the roots, biological matter and other organic material filtered out the suspended solids. Total suspended solids can have negative affects on CTWs because of plugging. Since in this study the majority of the TSS is due to VSS, the concern that plugging will occur over long term operation is reduced. Once filtered by the wetland, the VSS will decompose in the media of the wetland and the organics it releases will be consumed by the biological matter in the CTWs.

During the November 20th and January 15th sampling events both a TSS and VSS samples were collected from the effluent of the CTW. The results of this sampling event indicate that the suspended solids in the effluent of the constructed wetland are usually organic solids. This is due to the natural processes that are going on in the wetland. As biological matter dies and decomposes some of the matter will be released in the effluent water stream. Though Outfall 007 does not have a discharge limit for TSS or VSS, the wetland would able to meet TSS limits that are implemented at other outfalls at TN Ops North Plant, with a daily average of 20 mg/l and a daily max of 40 mg/l.

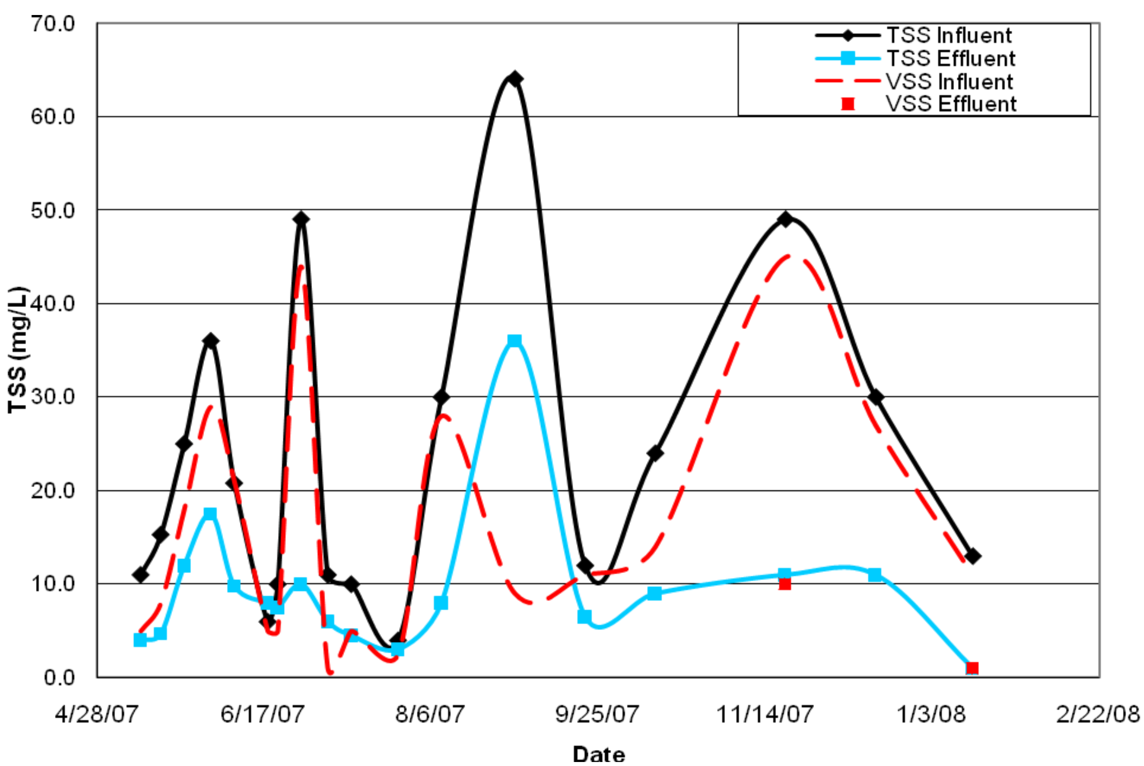


Figure (4.1) CTW TSS/VSS Sampling Results

2. pH

Figure (4.2) presents the changes in pH as water moved through the wetland. The discharge from outfall 007 must be with in the pH range of 6.0 – 9.0. The leachate has an average pH of 8.4 and is highest during the summer months. As Figure (4.2) indicates the effluent pH from the CTW was very stable with an average pH of 7.55, a standard deviation of 0.21 units, and did not fluctuate as drastically as the influent pH. The change in pH is due to the biological activity in the CTW such as nitrification. As the microbes nitrified the ammonia in the influent, free hydrogen is released into the water

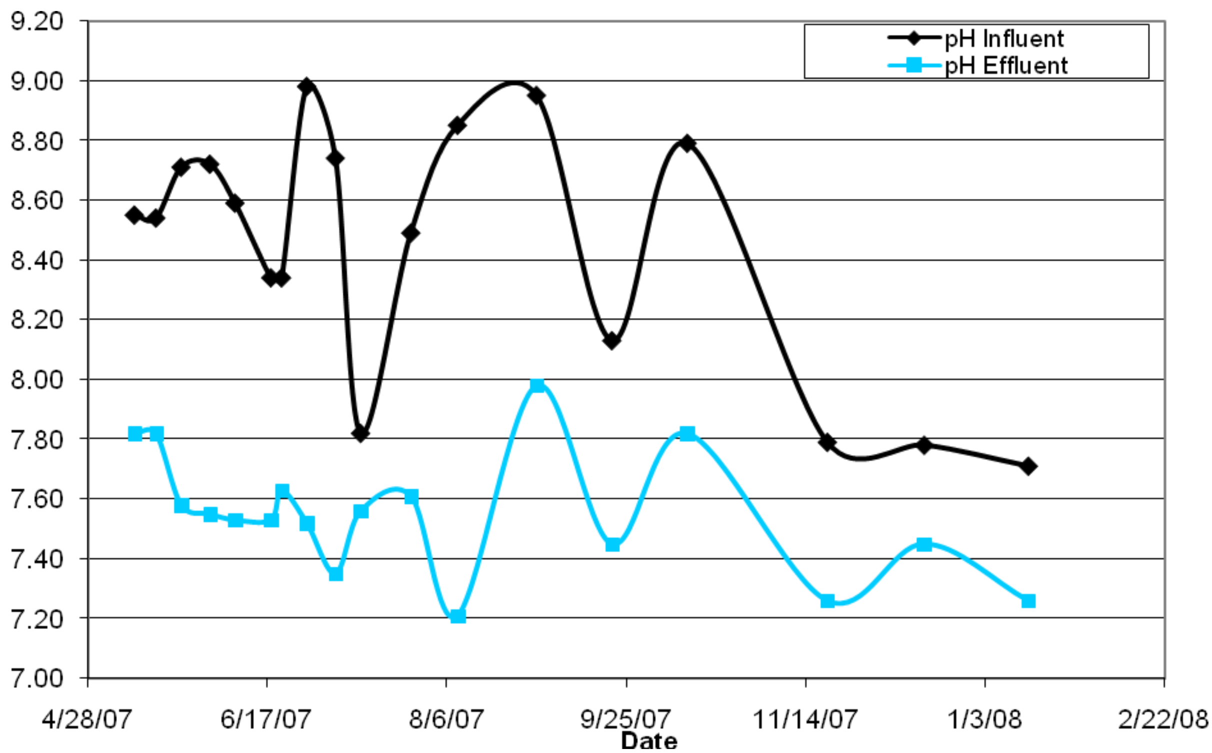


Figure (4.2) CTW pH Sampling Results

lowering the pH. The study data indicates that the constructed wetland would meet discharge limits at outfall 007 and that the influent pH is manageable by the wetland.

3. Temperature

Temperature was monitored in the CTW to determine its affects on biological activity. As shown in Figure (4.3) there was little change in temperature between the influent and effluent samples. Since the collection pond had a larger volume of water and is accentually ground water, its temperature did not fluctuate as quickly as the wetland. The ambient weather conditions had an affect on the CTW temperatures and during the winter months caused the upper portion of the wetland to freeze.

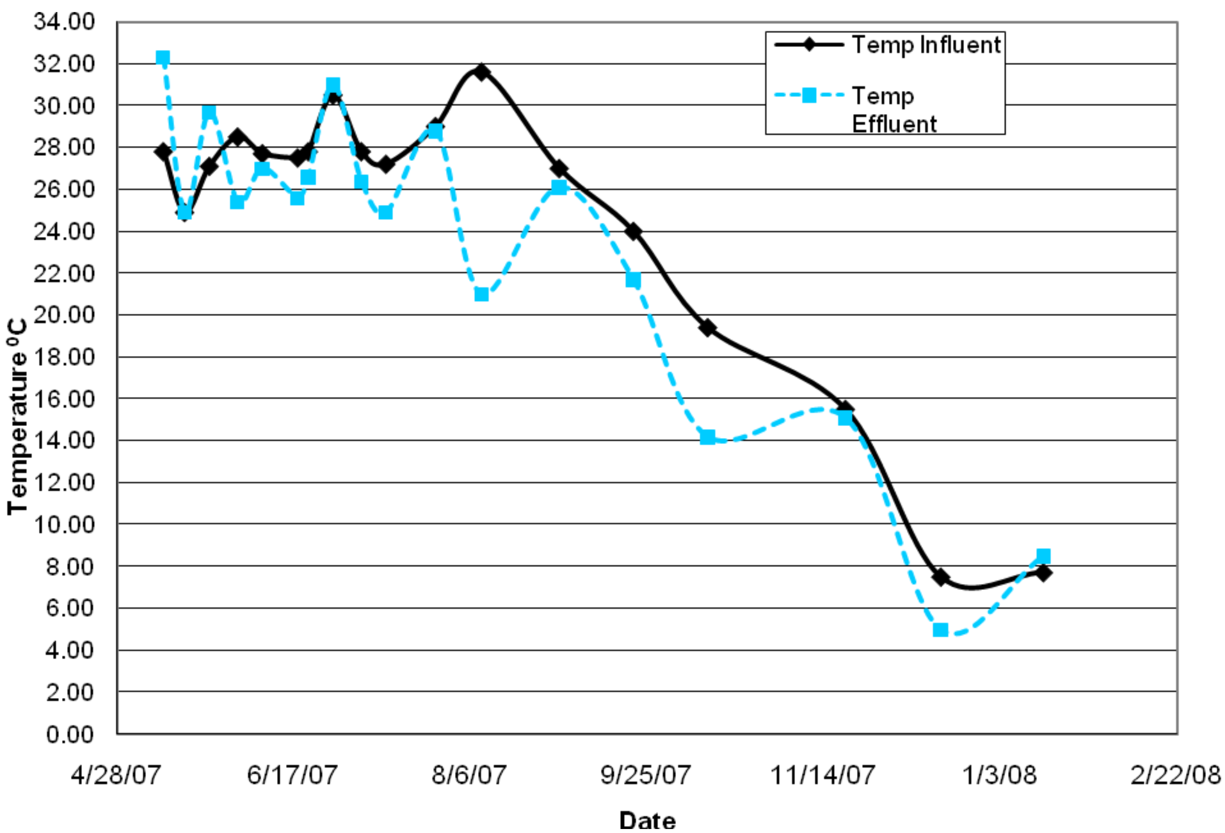


Figure (4.3) CTW Temperature Sampling Results

During sunny, warm weather the CTW would heat up quicker than the pond causing then effluent temperature to be higher than the influent leachate.

4. Dissolved Oxygen

Dissolved Oxygen was monitored in the influent and effluent of the wetland because many biological processes depend on oxygen as an electron donor. In this study it is assumed that the oxygen was consumed by biological activity in the wetland. Figure (4.4) presents the changes in influent and effluent dissolved oxygen. The data gap from the August 31st till the December 12th sampling event is due to failure in the dissolved oxygen meter.

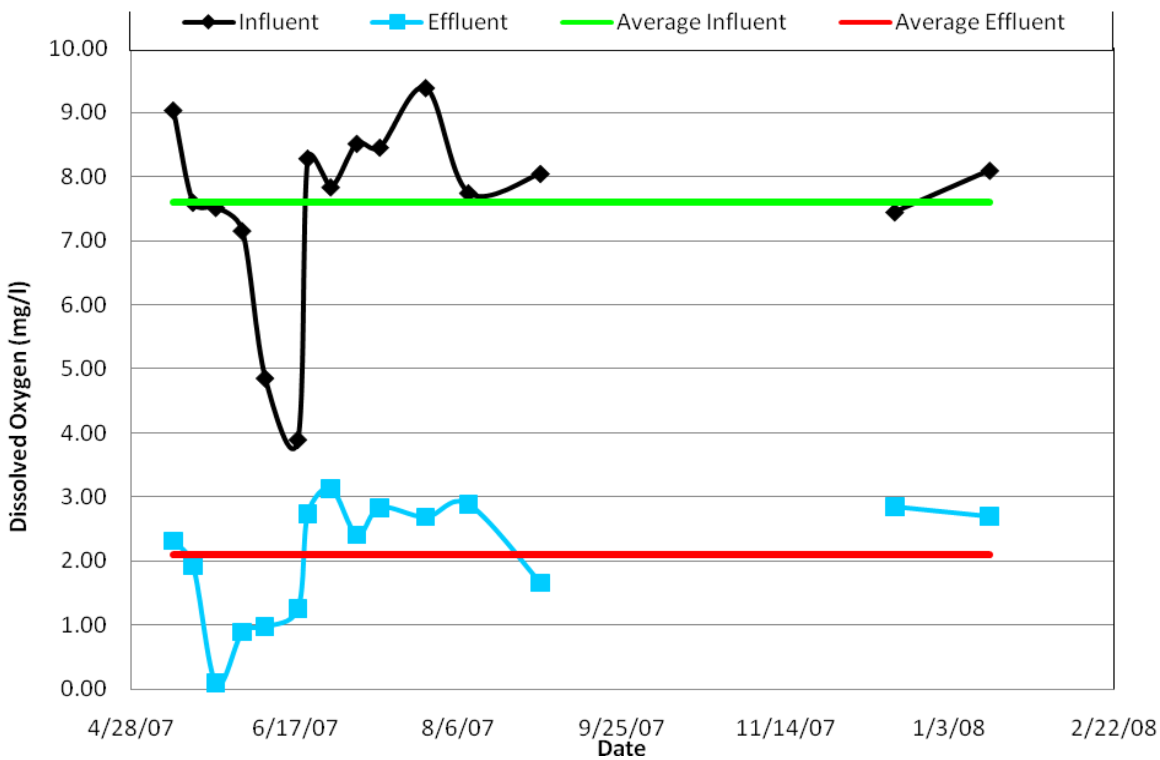


Figure (4.4) CTW Dissolved Oxygen Sampling Results

B. Constructed Treatment Wetland Nitrogen Sampling and Modeling

The three forms of nitrogen that were monitored during this study are ammonia, nitrate and nitrite. All analytical results were reported as total nitrogen, i.e. ammonia as nitrogen, and nitrate/nitrite were considered one species being reported together. The goal of the wetland was to remove ammonia from the influent leachate by nitrification. Nitrification oxidizes into nitrite and then nitrate through the following chemical reaction: (Henze 2002)

$$\frac{1}{6} NH_4^+ + \frac{1}{4} O_2 \rightarrow \frac{1}{6} NO_2^- + \frac{1}{6} H_2O + \frac{1}{3} H^+$$

$$\frac{1}{6} NO_2^- + \frac{1}{4} O_2 \rightarrow \frac{1}{2} NO_3^-$$

As stated earlier this process requires 4.6 grams of oxygen per gram of ammonia and can be limited by the dissolved oxygen concentration. In the process of denitrification the nitrate (NO_3) is biologically reduced to nitrogen (N_2). The process is heterotrophic, utilizes organic carbon and can utilize many different organic carbon species as a carbon sources. The general chemical process is as follow: (Henze 2002)

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2O$$

These processes have been presented because the results of the study indicate that both nitrification and denitrification occurred in the constructed wetland. Figures (4.5) and (4.6) present sampling results for ammonia and nitrate/nitrite respectively. The data for each species was analyzed and the Modified TIS Model developed by Kadlec and Wallace was applied to each data set. As a comparison of models, the Plug Flow

Model was also applied to the data set for both nitrification and denitrification. In utilizing the Modified TIS Model the first order rate constant was determined from the observed data. For the Plug Flow modeling, Equation (2.1), was modified as shown in Equation (4.1) and the first order rate constant was determined from the observed data. (Hammer, 1989) The modeling steps are further described later in this section.

Modified Plug Flow

$C_e = \exp[\ K_t\, t]\ \ C_0$ **(4.1)**

Where:

C_0 = Influent COD Concentration (mg/l)

C_e = Effluent COD Concentration (mg/l)

t = Hydraulic Residence Time (HRT) of the system (Days)

$t = \frac{Vv}{Q}$ **(4.2)**

Vv = Volume of Voids (liters)

Q = Flow Rate (liters/day)

K_t = Temperature – Dependent First Order Rate Constant

$K_t = K_{20}\ (1.1)^{(T-20)}$ **(4.3)**

K_{20}= Optimum Rate Constant

T = Temperature (^{0}C)

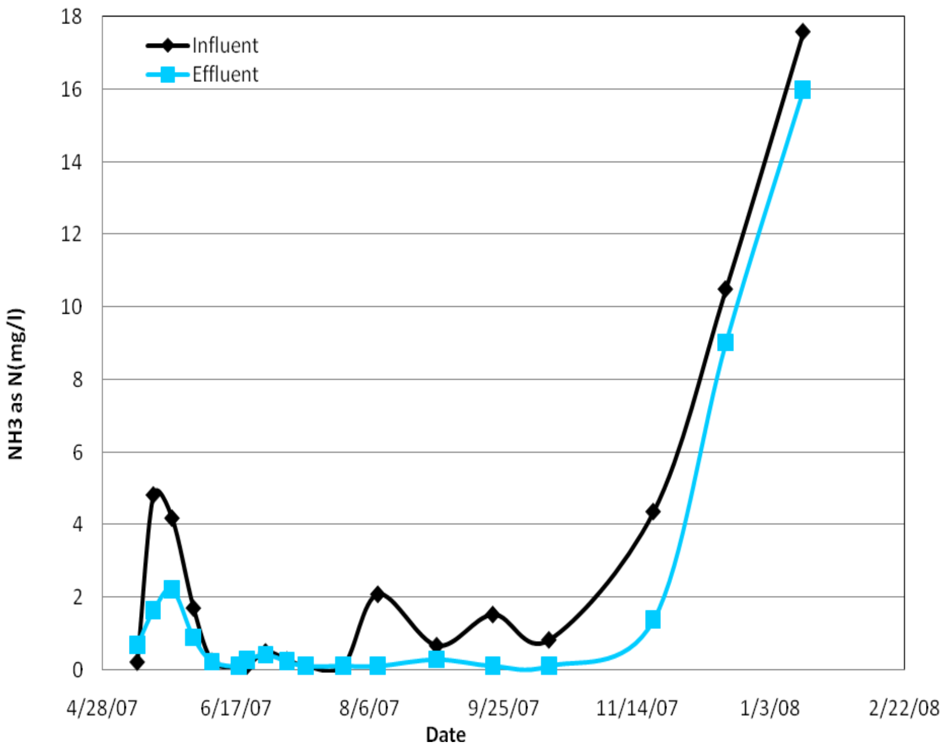


Figure (4.5) CTW Ammonia Sampling Results

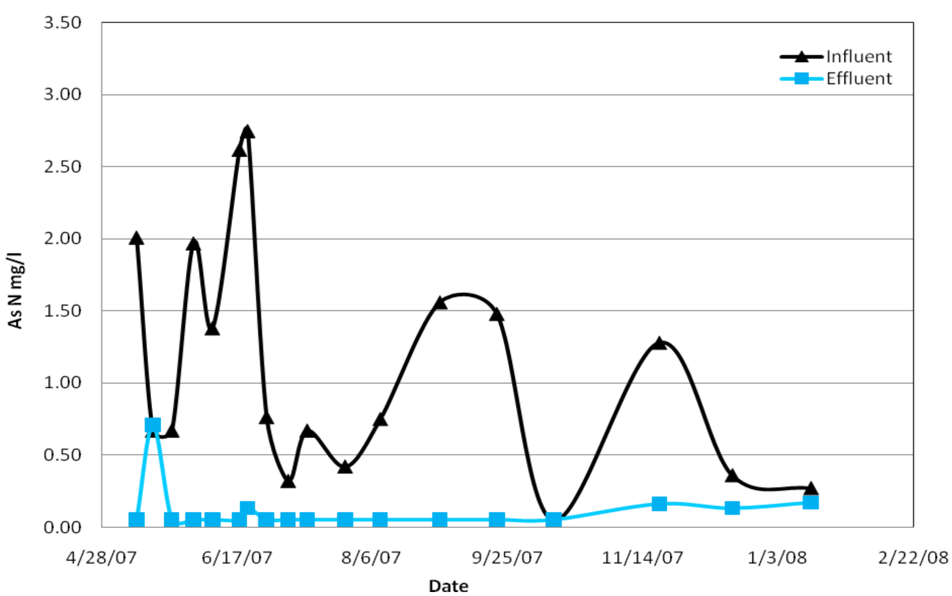


Figure (4.6) CTW Nitrate/Nitrite Sampling Results

For each nitrogen species, the modeling steps will be described and the data presented. For all Modified TIS modeling, the below design data was used. The upper number of tanks in series (P) was set at 5 and was determined from the data presented in Table 2**.**

Constructed Wetland Design Data

Q = 0.03 GPM = 163.64 l/day
Time (t) = 2.31 days
Assuming Cross Section Constant
Area (A) = 10.98 ft^2
q = 0.53 ft/day = 0.16 m/day
P = 5.00
V = 1134 Liters
V_v = 378 Liters
HRT = 2.31 days

1. Plug Flow Modeling Results

First ammonia and nitrate/nitrite removal was modeled using the Modified Plug Flow Model, Equation (4.1). Since this model is based on chemical oxygen demand (COD) all influent and effluent values of ammonia were converted to ammonia as COD by multiplying the concentration by 4.6. For nitrate/nitrite the standard Plug Flow Model was used, equation (2.1). The first step in using this model was to utilize the sampled data to find the first order reaction constant (K). It is assumed that the first order reaction constant (K), which was calculated from the sampling data, is the temperature corrected first order reaction constant (K_t). This (K_t) was then used to determine the first order reaction constant at 20 ^{0}C, (K_{20}). The average (K_{20}) was then found and this value was used to determine to (K_t) for each sampling event. This calculated (K_t) was then used in the Modified Plug Flow Model to determine the predicted effluent ammonia and nitrate/nitrite concentrations. Modeling data is presented in Table 7 for ammonia and Table 8 for nitrate/nitrite.

Table 7: Modified Plug Flow Ammonia Modeling Results

Sample Date	T (C)	C_0 mg/l	C_0 as COD	$C_{e\ (actual)}$ mg/l	$C_{e\ (actual)}$ as COD	$K_{t(actual)}$ (/day)	K_{20} (/day)	$K_{t(predicted)}$ (/day)	$C_{e\ (model)}$ as COD	$C_{e\ (model)}$ mg/l
5/11/07	27.80	0.21	0.97	0.68	3.13	-0.51	-0.24	0.43	0.35	0.08
5/17/07	24.90	4.82	22.17	1.63	7.50	0.47	0.29	0.33	10.36	2.25
5/24/07	27.10	4.18	19.23	2.21	10.17	0.28	0.14	0.41	7.52	1.64
6/1/07	28.50	1.70	7.82	0.88	4.06	0.28	0.13	0.46	2.68	0.58
6/8/07	27.70	0.23	1.07	0.22	1.03	0.02	0.01	0.43	0.40	0.09
6/18/07	27.50	0.10	0.46	0.10	0.46	0.00	0.00	0.42	0.17	0.04
6/21/07	27.80	0.10	0.46	0.27	1.24	-0.43	-0.20	0.43	0.17	0.04
6/28/07	30.50	0.49	2.25	0.41	1.89	0.08	0.03	0.56	0.62	0.13
7/6/07	27.80	0.27	1.23	0.23	1.06	0.06	0.03	0.43	0.45	0.10
7/13/07	27.20	0.10	0.46	0.10	0.46	0.00	0.00	0.41	0.18	0.04
7/27/07	29.00	0.11	0.52	0.10	0.46	0.06	0.02	0.49	0.17	0.04
8/9/07	31.60	2.08	9.57	0.10	0.46	1.31	0.43	0.62	2.26	0.49
8/31/07	27.00	0.66	3.04	0.28	1.29	0.37	0.19	0.40	1.20	0.26
9/21/07	24.00	1.52	6.99	0.10	0.46	1.18	0.80	0.30	3.48	0.76
10/12/07	19.40	0.82	3.77	0.10	0.46	0.91	0.96	0.19	2.40	0.52
11/20/07	15.50	4.36	20.06	1.38	6.35	0.50	0.76	0.13	14.70	3.20
12/17/07	7.50	10.50	48.30	9.02	41.49	0.07	0.22	0.06	41.78	9.08
1/15/08	7.50	17.60	80.96	16.00	73.60	0.04	0.14	0.06	70.04	15.23
						Average =	**0.206**			

Table 8: Plug Flow Model Nitrate/Nitrite Modeling Results

Sample Date	T (C)	C_0 mg/l	$C_{e\ (actual)}$ mg/l	$K_{t(actual)}$ (/day)	K_{20} (/day)	$K_{t(predicted)}$ (/day)	$C_{e\ (model)}$ mg/l
5/11/07	27.80	2.01	0.05	1.599	0.760	1.355	0.088
5/17/07	24.90	0.67	0.71	-0.025	-0.016	1.028	0.062
5/24/07	27.10	0.67	0.05	1.123	0.571	1.268	0.036
6/1/07	28.50	1.97	0.05	1.590	0.707	1.449	0.069
6/8/07	27.70	1.38	0.05	1.436	0.689	1.342	0.062
6/9/07	27.50	2.62	0.05	1.714	0.839	1.317	0.125
6/10/07	27.80	2.75	0.13	1.321	0.628	1.355	0.120
6/28/07	30.50	0.763	0.05	1.180	0.434	1.753	0.013
7/6/07	27.80	0.32	0.05	0.804	0.382	1.355	0.014
7/13/07	27.20	0.67	0.05	1.123	0.566	1.280	0.035
7/27/07	29.00	0.42	0.05	0.921	0.391	1.519	0.013
8/9/07	31.60	0.75	0.05	1.172	0.388	1.947	0.008
8/31/07	27.00	1.56	0.05	1.489	0.764	1.256	0.086
9/21/07	24.00	1.48	0.05	1.467	1.002	0.943	0.167
10/12/07	19.40	0.05	0.05	0.000	0.000	0.609	0.012
11/20/07	15.50	1.28	0.16	0.900	1.382	0.420	0.486
12/17/07	7.50	0.36	0.13	0.441	1.451	0.196	0.229
1/15/08	7.50	0.27	0.17	0.200	0.659	0.196	0.172
				Average =	**0.644**		

2. Modified Tank in Series Model Results

Next ammonia and nitrate/nitrite removal was modeled using the Modified TIS Model, Equation (2.3). The first step in using this model was to utilize the sampled data to find the first order reaction constant (K). It is assumed that the first order reaction constant (K), which was calculated from the sampling data, is the temperature corrected first order reaction constant (K_t). This (K_t) was then used to determine the first order reaction constant at 20 ^{0}C, (K_{20}). The average (K_{20}) was then found and this value was used to determine to (K_t) for each sampling event. This calculated (K_t) was then used in the Modified TIS Model to determine the predicted effluent ammonia and nitrate/nitrite concentrations. Modeling data is presented in Table 9 for ammonia and Table 10 for nitrate/nitrite.

Table 9: TIS Model Ammonia Modeling Results

Sample Date	C_i (mg/l)	$C_{e\ (Actual)}$ (mg/l)	C/C_i	K_t (m/day)	Temperature (^0C)	K_{20} (m/day)	K_t (m/day)	$C_{e\ (Modeled)}$ (mg/l)
5/11/2007	0.21	0.68	3.238	-0.168	32.3	-0.052	0.454	0.02
5/17/2007	4.82	1.63	0.338	0.194	24.9	0.121	0.224	1.40
5/24/2007	4.18	2.21	0.529	0.109	29.7	0.043	0.354	0.67
6/1/2007	1.70	0.882	0.519	0.112	25.4	0.067	0.235	0.47
6/8/2007	0.23	0.224	0.966	0.006	27	0.003	0.274	0.05
6/18/2007	0.10	0.1	1.000	0.000	25.6	0.000	0.240	0.03
6/21/2007	0.10	0.27	2.700	-0.144	26.6	-0.077	0.263	0.02
6/28/2007	0.49	0.41	0.837	0.029	31	0.010	0.401	0.06
7/6/2007	0.27	0.23	0.861	0.024	26.4	0.013	0.258	0.07
7/13/2007	0.10	0.1	1.000	0.000	24.9	0.000	0.224	0.03
7/27/2007	0.11	0.1	0.877	0.021	28.8	0.009	0.325	0.02
8/9/2007	2.08	0.1	0.048	0.668	21	0.607	0.154	0.86
8/31/2007	0.66	0.28	0.424	0.150	26.1	0.084	0.251	0.17
9/21/2007	1.52	0.1	0.066	0.579	21.7	0.492	0.165	0.59
10/12/2007	0.82	0.1	0.122	0.419	14.2	0.728	0.081	0.51
11/20/2007	4.36	1.38	0.317	0.207	15.1	0.330	0.088	2.59
12/17/2007	10.50	9.02	0.859	0.025	5	0.103	0.034	8.55
1/15/2008	17.60	16	0.909	0.015	8.5	0.046	0.047	13.23
					Average =	**0.140**		

Table 10: TIS Model Nitrate/Nitrite Modeling Results

Sample Date	C_i (mg/l)	$C_{e\ (Actual)}$ (mg/l)	C/C_i	K_t (m/day)	Temperature (^0C)	K_{20} (m/day)	K_t (m/day)	$C_{e\ (Modeled)}$ (mg/l)
5/11/2007	2.01	0.05	0.025	0.875	32.3	0.271	1.167	0.02
5/17/2007	0.67	0.71	1.060	-0.009	24.9	-0.006	0.576	0.04
5/24/2007	0.67	0.05	0.075	0.544	29.7	0.216	0.911	0.01
6/1/2007	1.97	0.05	0.025	0.868	25.4	0.519	0.605	0.12
6/8/2007	1.38	0.05	0.036	0.753	27	0.387	0.704	0.06
6/18/2007	2.62	0.05	0.019	0.966	25.6	0.566	0.616	0.15
6/21/2007	2.75	0.13	0.047	0.673	26.6	0.359	0.678	0.13
6/28/2007	0.76	0.05	0.066	0.580	31	0.203	1.031	0.01
7/6/2007	0.32	0.05	0.156	0.360	26.4	0.195	0.665	0.02
7/13/2007	0.67	0.05	0.075	0.544	24.9	0.341	0.576	0.04
7/27/2007	0.42	0.05	0.119	0.424	28.8	0.183	0.836	0.01
8/9/2007	0.75	0.05	0.067	0.575	21	0.523	0.398	0.10
8/31/2007	1.56	0.05	0.032	0.792	26.1	0.443	0.646	0.08
9/21/2007	1.48	0.05	0.034	0.775	21.7	0.659	0.425	0.18
10/12/2007	0.05	0.05	1.000	0.000	14.2	0.000	0.208	0.02
11/20/2007	1.28	0.16	0.125	0.413	15.1	0.658	0.227	0.37
12/17/2007	0.36	0.13	0.361	0.181	5	0.755	0.087	0.22
1/15/2008	0.27	0.17	0.630	0.078	8.5	0.232	0.121	0.13
					Average	**0.361**		

3. Modeling Comparison

Figure (4.7) and (4.8) is a comparison between the modeled data and the actual sampled data. The influent ammonia varied greatly during the operation of the constructed wetland, with a range of non-detectable (less than 0.1 mg/l) to a 17 mg/l. The root mean square error (RMSE) was used to determine the accuracy of each model. As Table 11 indicates, the Plug Flow Model is the more accurate model for ammonia results do to its low RMSE value. For nitrate/nitrite the RMSE indicates that the two models have a similar level of accuracy. For both models, the negative and zero values of the first order reaction constant were included in all calculations. This inclusion increased the accuracy of the models by lowering the RMSE value. The determination of whether the pilot unit was a Plug Flow or TIS will be made in the conclusion section of this paper.

Table 11: Root Mean Square Error

Ammonia						**Nitrate/Nitrite**				
		Modeling Results		Square Error			Modeling Results		Square Error	
Date	$C_{e\ (Actual)}$	TIS	Plug	TIS	Plug	C_e (actual)	TIS	Plug	TIS	Plug
	(mg/l)	(mg/l)	(mg/l)			mg/l	(mg/l)	(mg/l)		
5/11/07	0.68	0.02	0.08	0.43	0.36	0.05	0.02	0.09	0.00	0.00
5/17/07	1.63	1.40	2.25	0.05	0.39	0.71	0.04	0.06	0.44	0.42
5/24/07	2.21	0.67	1.64	2.37	0.33	0.05	0.01	0.04	0.00	0.00
6/1/07	0.882	0.47	0.58	0.17	0.09	0.05	0.12	0.07	0.00	0.00
6/8/07	0.224	0.05	0.09	0.03	0.02	0.05	0.06	0.06	0.00	0.00
6/18/07	0.1	0.03	0.04	0.01	0.00	0.05	0.15	0.13	0.01	0.01
6/21/07	0.27	0.02	0.04	0.06	0.05	0.13	0.13	0.12	0.00	0.00
6/28/07	0.41	0.06	0.13	0.12	0.08	0.05	0.01	0.01	0.00	0.00
7/6/07	0.23	0.07	0.10	0.03	0.02	0.05	0.02	0.01	0.00	0.00
7/13/07	0.1	0.03	0.04	0.01	0.00	0.05	0.04	0.03	0.00	0.00
7/27/07	0.1	0.02	0.04	0.01	0.00	0.05	0.01	0.01	0.00	0.00
8/9/07	0.1	0.86	0.49	0.58	0.15	0.05	0.10	0.01	0.00	0.00
8/31/07	0.28	0.17	0.26	0.01	0.00	0.05	0.08	0.09	0.00	0.00
9/21/07	0.1	0.59	0.76	0.24	0.43	0.05	0.18	0.17	0.02	0.01
10/12/07	0.1	0.51	0.52	0.17	0.18	0.05	0.02	0.01	0.00	0.00
11/20/07	1.38	2.59	3.20	1.46	3.30	0.16	0.37	0.49	0.04	0.11
12/17/07	9.02	8.55	9.08	0.22	0.00	0.13	0.22	0.23	0.01	0.01
1/15/08	16	13.23	15.23	7.65	0.60	0.2	0.13	0.17	0.00	0.00
		Mean Square Error		0.76	0.33		Mean Square Error		0.0298	0.0314
		Root Mean Square Error =		**0.87**	**0.58**		**Root Mean Square Error =**		**0.17**	**0.18**

Figure 4.7 Modeling Vs Actual Comparison for Nitrate/Nitrite

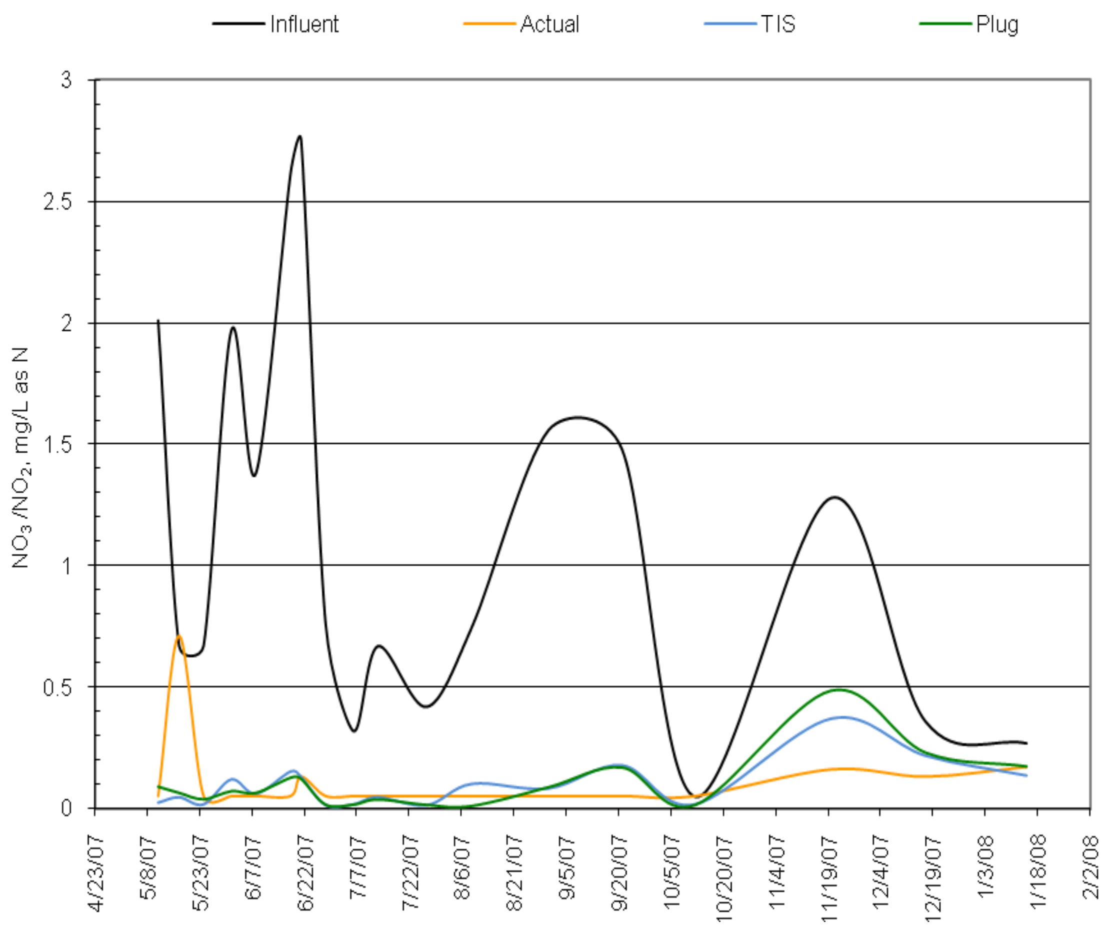
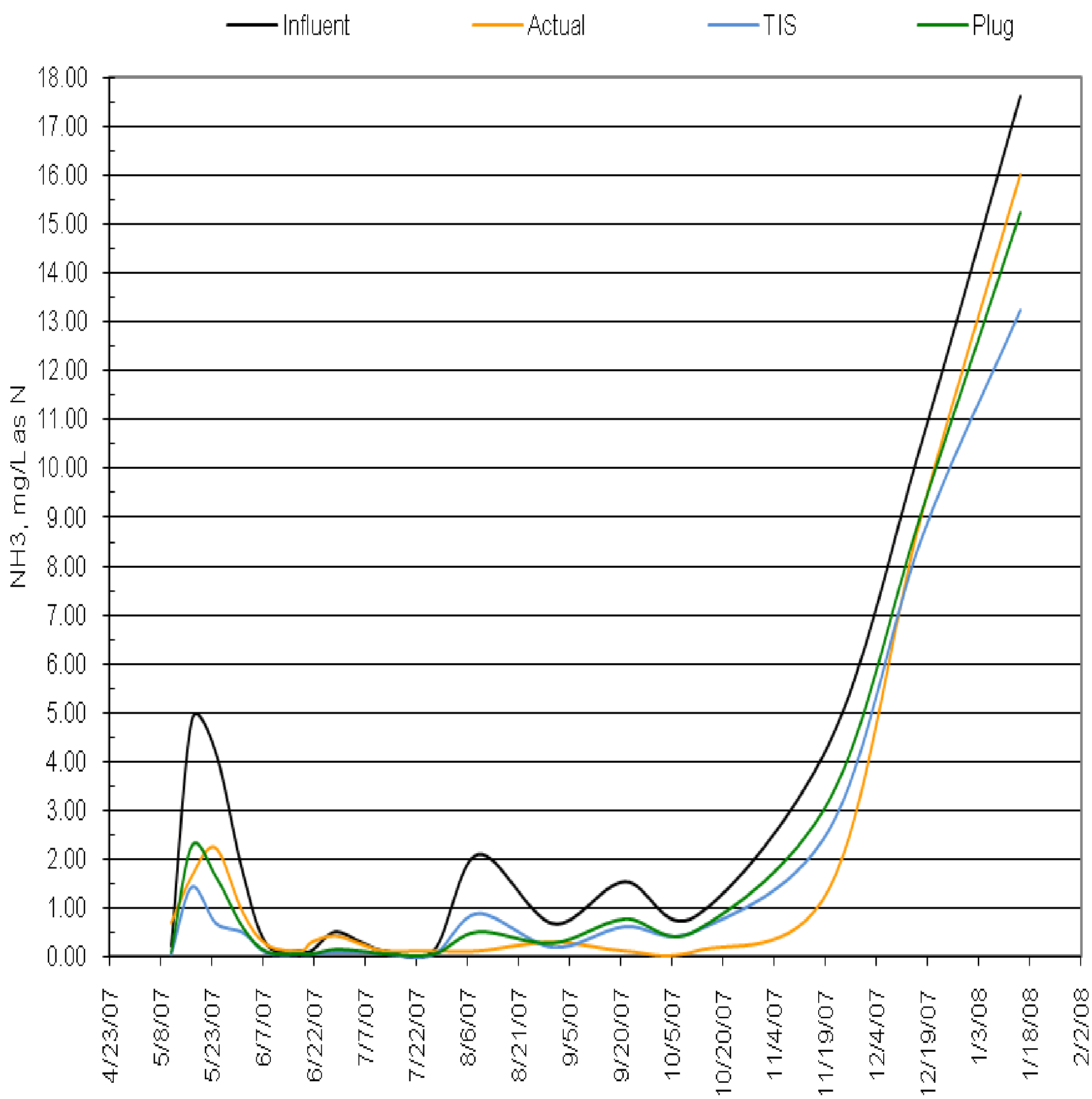


Figure 4.8 Modeling Vs Actual Comparison for Ammonia



C. Natural Media Filter Results

The purpose of the NMF that was installed at Outfall 007 was to remove PCB contamination from the leachate. Other sampling was performed on the NMF to monitor its affect on the effluent stream to insure that the NMF would not cause failure of other discharge parameters. First the sampling results of other parameters will be presented followed by the main focus of the study the PCB sampling results. Results of other parameters sampled will not be presented because there was zero, to little change between influent and effluent concentrations.

1. Suspended Solids and Color

Figure (4.9) displays the suspended solids sampling results during the pilot study. As indicated in Figure (4.9), the majority of the suspended solids are due to volatile suspended solids in both the influent and the effluent. The influent VSS is due to algae in the pond and the VSS in the effluent is due to organic matter being released from the NMF. Until the pump was installed, to control the influent flow rate, there were large fluctuations in the flow rate, 0.05 gpm to 1 gpm. This large fluctuation in flow, coupled with the NMF being designed as an up-flow unit, did not allow the mushroom compost to settle and caused it to continually release material, VSS, in the effluent. Once the pump was installed, in July, the composted settled and the suspended solid effluent results became more constant. The influent flow fluctuations also caused the NMF to release color for longer time period than other pilots as indicated in Figure (4.10). Most other NMF pilots stopped releasing colored effluent after the first few days, but the TN unit was still releasing color two months after start up. This was also the first pilot up-flow unit Alcoa had operated.

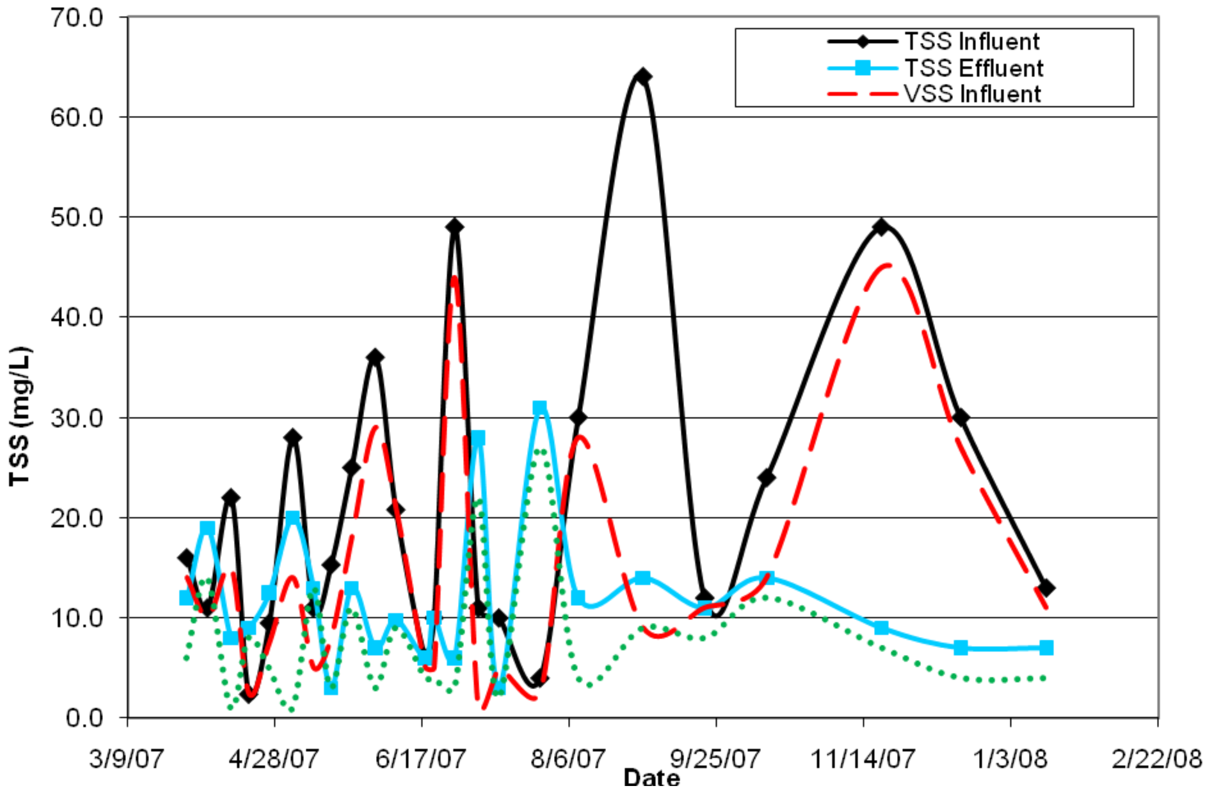


Figure (4.9) Suspended Solids Sampling Results

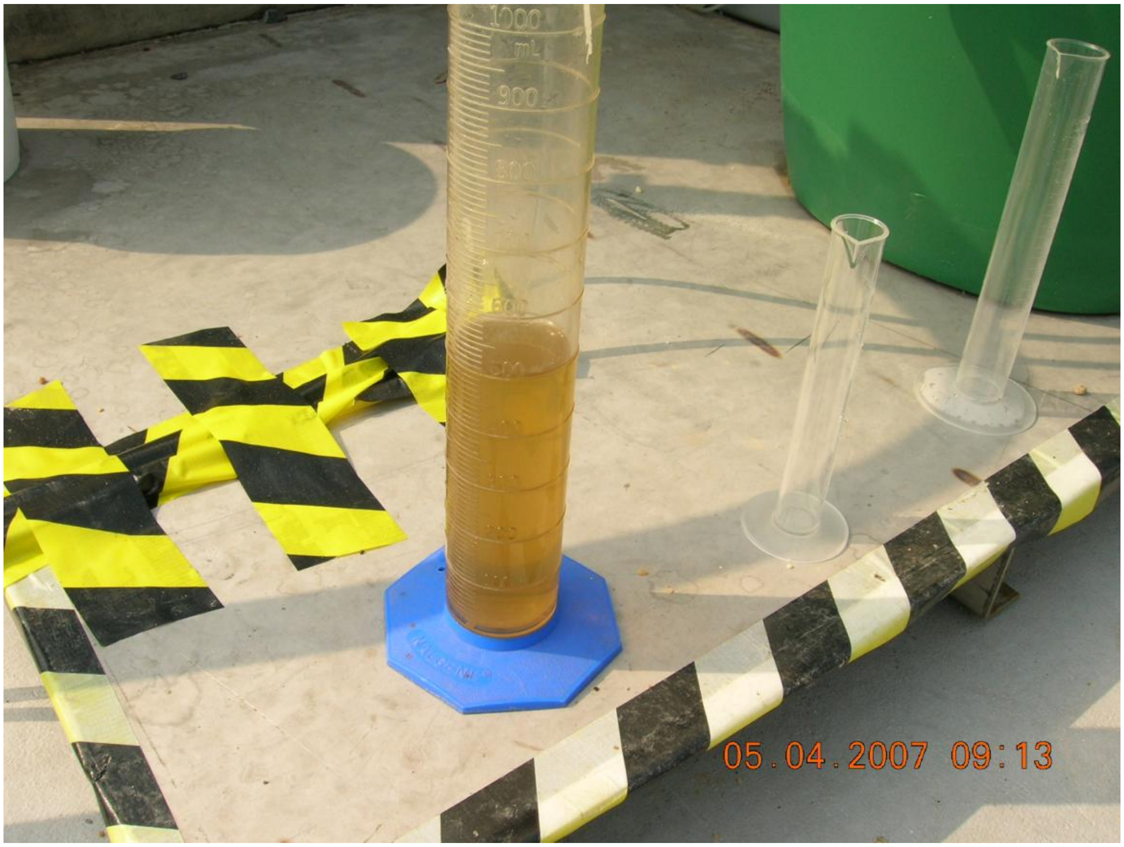


Figure (4.10) NMF Effluent Color on May 4, 2007

2. Dissolved Oxygen and pH Sampling Results

The sampling results indicated that the unit was an oxidizing atmosphere and consumed oxygen, Figure (4.11). This consumption of oxygen is due to both biological oxygen consumption and chemical oxygen consumption. One of the benefits of NMF is that in the compost used, there is both humic material and microbes. The presences of these two materials/organisms allows for oxidizing of pollutants into inert compounds or bonding of pollutants to the media. This large consumption in dissolved oxygen indicates that the NMF is performing as expected, but that effluent will be low in

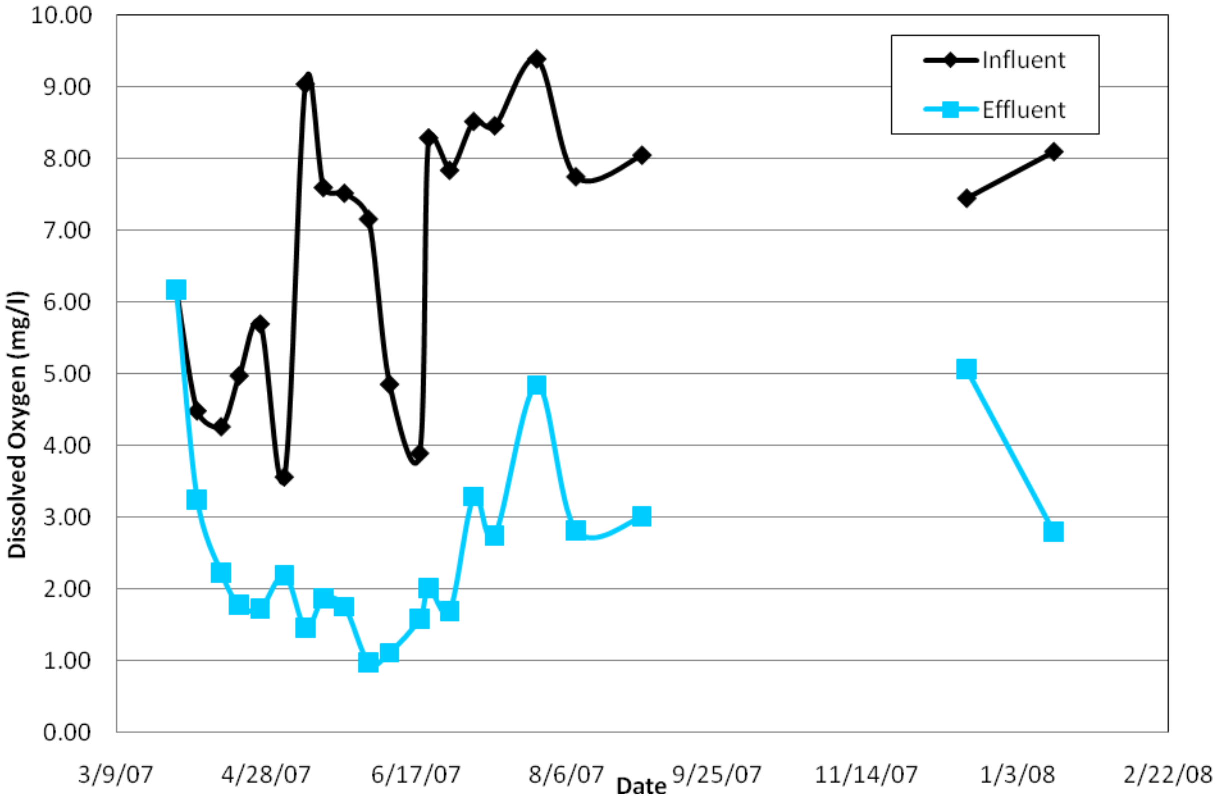


Figure (4.11) NMF Dissolved Oxygen Sampling Results

dissolved oxygen. As with the CTW, the NMF slightly reduced the pH of the leachate from an average influent of 8.4 to an average effluent of 7.6 with little fluctuation.

3. Natural Media Filter Nitrogen Results

Figures (4.12) and (4.13) present the sampling results of ammonia and nitrate/nitrite respectively. As Figure (4.12) indicates, the NMF was not able to reduce ammonia and during the startup period it increased the ammonia levels in the effluent. This increase is caused by the mushroom compost and what it consists of, cow manure.

As the manure decomposes it releases nutrients such as ammonia. As the flow fluctuated the ammonia that was being produced from decomposing manure would be flushed out. A low oxygen, possibly anoxic environment may have contributed to the nitrate/nitrite reduction as indicated in Figure (4.13). The upper regions of the NMF were most likely anaerobic and denitrifing microbes may have been active to reduce the nitrate/nitrite levels in the leachate. Nitrate/Nitrite may also have been reduced to ammonia causing the increase in ammonia. Figure (4.12) and Figure (4.13) do not directly show that this reduction was occurring and with the many source of nitrogen present in the NMF, the current data does not allow a mass balance to be performed.

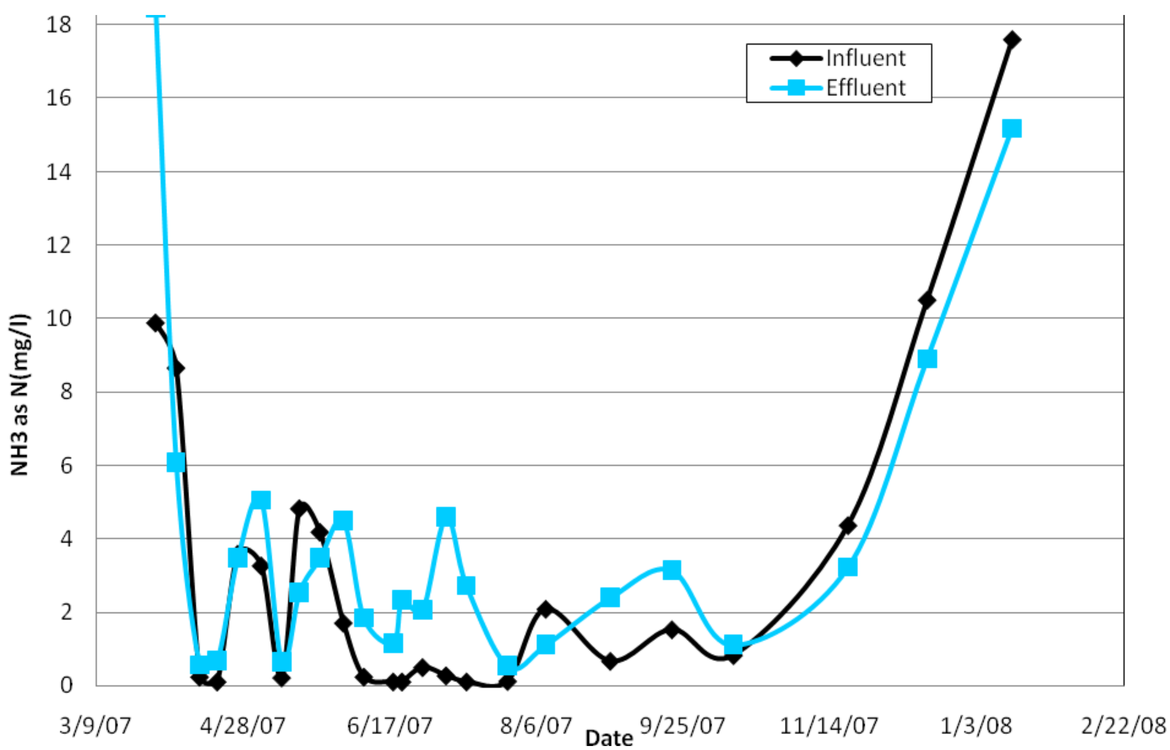


Figure (4.12) NMF Ammonia Sampling Results

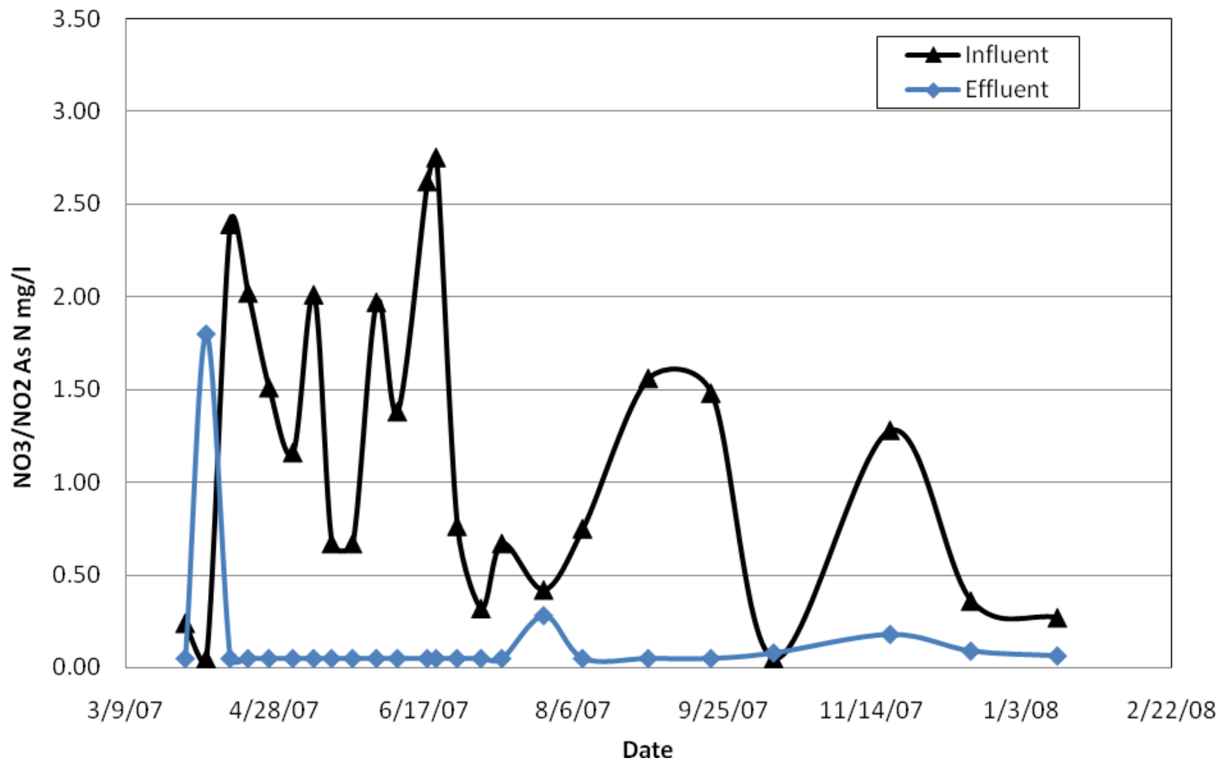


Figure (4.13) NMF Nitrate/Nitrite Sampling Results

4. Natural Media Filter PCB Removal

The analytical method used to test for PCBs had a detection limit of two hundred parts per trillion and PCBs are not always present at current detection levels in the landfill leachate. It was not until the last few months of the pilot study that PCBs became detectable in the influent leachate. Historical sampling records of Outfall 007 indicate that PCBs are usually present in the leachate when high levels of oil and grease are present. This study was focused on the ability of a NMF to removed PCBs from the leachate and not on the hydraulics of the landfill that produces the leachate, but a statement must be made to account for this large and sudden increase in PCB concentration.

During the pilot study East Tennessee was in an extreme drought. The landfill that feeds the Outfall 007 leachate pond is essentially a covered bathtub. The PCB contaminated oils are mostly free phase oils that float on top of the bathtub water. As the drought worsened and the water levels in the landfill/bathtub lowered; the free phase PCB contaminated oils reached the seeps that feed the leachate collection pond. At times during the study large sheens of free phase oil were observed on the pond. This oil is removed from the pond by an oil skimmer, but some of the oil does become emulsified or distributed in the water column contaminating the leachate. The drought conditions experience during the study and their affect on the pilot will be discussed in the conclusion section.

Table 12 presents the PCB sampling data and information used to calculate the PCB loading on the NMF. As Table 12 shows there were no detectable PCBs until the November 20th sampling date. The 6.4 mg/day/ft^2 PCB loading rate is nine times higher than the recommend loading rate at a flow rate of 0.2 gpm. The unit was able to absorb the high influent PCB concentration and influent levels started falling back into the expected range during the following sampling events. Between the December and January sampling events the NMF had frozen completely and the unit had to be shut down. Once temperature warmed up and the unit was restarted, PCB breakthrough occurred as shown in the January 15 sampling event. It was assumed that this breakthrough may have been due to short circuiting through flow channels that may have formed when the compost was frozen. After allowing the unit to run for two months

Table 12: NMF PCB Sampling Results and Loading Rates

Sample Date	Est. Flow gpm	HLR (gpm/ft^{2})	Interval Between Sampling (Days)	Total PCB Influent (ug/L)	Influent PCB Loading (mg/day/ft^{2})	Total PCB Effluent (ug/L)	Effluent PCB Loading (mg/day/ft^{2})
3/22/07	0.25	0.019	0				
3/29/07	0.22	0.017	7	<0.2		<0.2	
4/5/07	0.19	0.014	7	<0.2		<0.2	
4/13/07	0.24	0.018	8	<0.2		<0.2	
4/19/07	0.25	0.019	6	<0.2		<0.2	
4/26/07	0.42	0.032	7	<0.2		<0.2	
5/4/07	0.13	0.010	8	<0.2		<0.2	
5/11/07	0.29	0.022	7	<0.2		<0.2	
5/17/07	0.18	0.014	6	<0.2		<0.2	
5/24/07	0.75	0.056	7	<0.2		<0.2	
6/1/07	0.53	0.039	8	<0.2		<0.2	
6/8/07	0.19	0.014	7	<0.2		<0.2	
6/18/07	0.53	0.039	10	<0.2		<0.2	
6/21/07	0.53	0.039	3	<0.2		<0.2	
6/28/07	0.05	0.004	7	<0.2		<0.2	
7/6/07	0.79	0.059	8	<0.2		<0.2	
7/13/07	0.42	0.032	7	<0.2		<0.2	
7/27/07	0.29	0.022	14	<0.2		<0.2	
8/9/07	0.26	0.019	13	<0.2		<0.2	
8/31/07	0.05	0.004	22	<0.2		<0.2	
9/21/07	0.17	0.013	21	<0.2		<0.2	
10/12/07	0.19	0.014	21	<0.2		<0.2	
11/20/07	0.25	0.019	39	62.20	6.417	<0.2	
12/17/07	0.20	0.015	27	15.70	1.249	<0.2	
1/15/08	0.21	0.016	29	16.00	1.376	1.170	0.101
3/31/2008	0.21	0.016	76	4.41	0.379	1.045	0.090

an additional sample was collected on March 31, 2008 to determine if the units had recovered from the January sampling event. This sample showed that the unit was still releasing PCBs. At this point the unit was shut down and the Alcoa EHS Technology Group took core samples of the compost. The samples were taken at different levels and locations across the compost. After analyzing the samples for total PCBs, Table 13 was developed to represent the total mass of PCBs applied to the unit, the estimated total amount of PCBs present in the compost, and the total mass of PCBs that passed through the unit.

Table 13: PCB Mass Balance

TOTAL PCBs IN MEDIA =	3.16	g
TOTAL PCBs INFLUENT INPUT =	4.73	g
TOTAL PCBs EFFLUENT =	0.13	g
TOTAL PCBs DIFFERENCE =	1.44	g

The data that was collected was not sufficient to determine the adsorption capacity of the natural media. Once PCBs were detected in the influent, the sampling frequency should have been increase to acquire enough data to model the adsorption capacity of the NMF. With the NMF being a constant flow system; a separate, no flow system would need to be developed to allow for the PCB concentration to equilibrate between the two medias to properly model the adsorption characteristics of the NMF.

CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

A. Constructed Treatment Wetland Conclusions

The TN pilot CTW achieved mixed results in meeting its purpose of removing ammonia from the leachate. It was able to treat low levels of ammonia, but had little effect on high levels of ammonia in the leachate. The highest levels of ammonia were seen in the winter months when microbial activity would be at its slowest. Also, there was not enough dissolved oxygen present in the influent water to nitrify all the influent ammonia. Though chlorine levels in the pond are kept low, many times during the study the pond would be shocked with sodium hypochloride to kill algae blooms. These “shock” events most likely would also have killed some of the nitrifying bacteria present in the CTW.

Nitrate/Nitrite are not a constituents of concern at Outfall 007 and were only monitored to determine if nitrification was occurring. The data gained from the study and information retrieved during the literary review indicated that subsurface wetlands are more suitable for denitrification due to their anaerobic conditions. Since the sampling results indicated that denitrification was occurring in the pilot wetland, the nitrate/nitrite removal was modeled in this study. The nitrate/nitrite levels were low in the influent levels, but there was enough change between the influent and effluent samples to justify using the data to test the accuracy of the models. As with nitrification, both the “shocking” of the collection pond and the low temperatures would have had an affect on the ability of the CTW to process nitrate/nitrite.

After utilizing both the Modified TIS Model and Plug Flow Model to analyze the data from the CTW it can be concluded that the unit operated as a Plug Flow unit. The Plug Flow Modeling predicted results were closer to the actual values than the Modified TIS Model and had a lower RMSE. The size of the unit coupled with the short time of operation also helped to conclude that water most likely moved through the wetland in a plug and that “tanks” did not develop in the wetland. Though this pilot unit is better modeled as a Plug Flow unit, the Modified TIS Model would be better to use in full scale design. If the average, minimum, and maximum first order reaction constants calculate during this study are used to find the area needed for a full scale CTW; the Modified TIS Model would require the most area at the minimum observed reaction rate, Table 14. The minimum first order reaction rate is the most important rate because this is when the wetland is the least efficient and if high levels of pollutants, in this case ammonia, are present effluent limits will not be achieved. The Modified TIS Model is more conservative than the Plug Flow Model and it better represents the many processes that occur in CTWs that affect its pollutant removal capabilities.

The reaction constants that were used in the calculation of Table 14 are the calculated K_t values from the modeling results. The design criteria for a full scale unit that would remove all levels of ammonia observed during the pilot study is listed below and was utilized to develop Table 14:

Q =	5.00	GPM	C_{in} =	17.0 mg/l
Q =	27.25	m^3/d		
P =	5.00		C_{out} =	0.1 mg/l

Table 14: Full Scale CTW Sizing Comparison

Modified TIS Model			
	k (m/day)	q (m/d)	A (m^2)
Average	0.23	0.03	1080.01
Min	0.03	0.00	7266.12
Max	0.45	0.05	538.62
Plug Flow Model			
	K (/day)	t (days)	A (m^2)
Average	0.37	14	381.89
Min	0.06	82	2231.16
Max	0.62	8	224.37

This pilot showed that a CTW has the potential to be a low cost, low maintenance option for Outfall 007, but that a large area would be needed to ensure its ability to handle the high levels of ammonia released from the landfill.

B. Natural Media Filter Conclusions

The Tennessee NMF could be considered a success. The unit was effective at removing PCBs at loading nine times higher than designed. The breakthrough at the end of the study does not indicate that the unit failed. This breakthrough was not caused by the failure of natural media to filter PCBs, but by the extreme events, freezing and high loading rate, that the unit experienced. Once the unit froze and in turn defrosted flow channels almost certainly formed in the compost. Since the unit was an up-flow unit the flow channel most likely never closed in-between the January and March 2008 sampling events. After freezing, the unit should have been drained and the compost remixed to close any flow channels that may had developed. Though there was no breakthrough of PCBs during the November 20th sampling event, this extremely high loading rate may have consumed a large portion of the compost adsorption capacity. This reduced adsorption capacity is indicated in the following December sampling event where the PCB loading rate was within the designed range, but effluent PCBs were detected.

The Tennessee NMF was the first up – flow unit operated by Alcoa Inc. This unit showed that this design has the potential to be used in other scenarios and may be able to handle high loading rates than down flow units. The study showed that up-flow units will require very steady flow rates to operate properly and that it will take longer for the compost to stabilize. This study also indicates, especially for up-flow units, that NMF may not be applicable in all situations as a final treatment step. If discharge parameters include dissolved oxygen and nitrogen limits, a NMF would not be able to meet these limits. Final aeration or treatment would be needed to meet these limits. The study did accomplish its goal of providing more data on natural media's ability to filter PCBs and indicated that with further studies may be a low cost, long term treatment solution at Outfall 007.

C. Oil and Grease Removal

A contaminate of concern that was not discussed, but monitored during the study was oil and grease. Due to the lack of literature on the ability of both NMF and CTW to remove oil and grease; only observation can be made on their ability to remove oil and grease. Figure (5.1) represent the oil and grease sampling results for both the NMF and CTW. As with the PCB concentrations, the spike in oil and grease concentration came at the end of the study and was due to the drought conditions. As Figure (5.1) indicates, both the NMF and the CTW were effective at removing the oil and grease form the leachate. During the September sampling event, influent and effluent oil and grease values were equal for the CTW. These results are most likely due to a sampling error. Both the NMF and CTW effluent would meet discharge limits for oil and grease at Outfall 007.

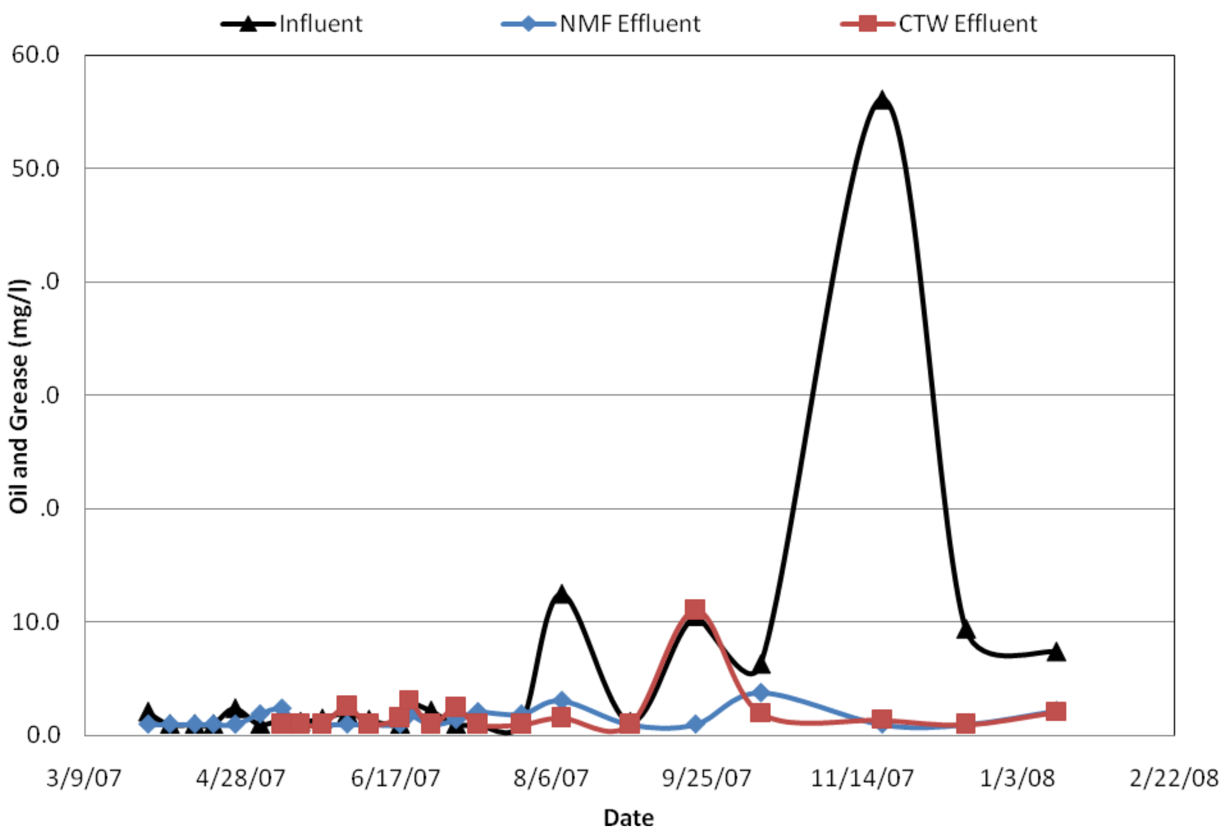


Figure (5.1) Oil and Grease Removal

It is assumed that oil and grease is removed in the CTW by microbial activity similar to a trickling filter. There is little data available to prove this assumption and without knowing the chemical composition of the oil in the leachate it is hard to determine how the oil is biodegraded. The oil may also have been filtered by the biological mass present in the wetland and biodegraded slowly. If biodegradation was occurring in the CTW it would consume dissolved oxygen and the microbes oxidizing the oil would have competed with nitrifying bacteria, limiting their ability to reduce ammonia.

It can be assumed that the NMF filtered the oil and grease from the leachate as any other mechanical media would. As with mechanical filter, the oil and grease seemed to cause the NMF to blind has indicated by increase head difference between the two sides. The NMF sampling results showed that it is very affective at removing oil and grease from wastewater and at low levels there may not be a large affect on the life of the filter. NMF are not designed to handle higher levels of oil and grease like those experienced during the end of the study and though they will remove the oil, it will greatly jeopardize the life of the filter.

D. Recommendations

The study of the Tennessee pilot NMF and CTW have shown that there is potential for this system to be implemented as a full scale treatment option for Outfall 007. Before full scale implementation can be started, adjustments to the Tennessee pilot should be made and more data should be collected. Since the two systems were run in parallel and not in series the pilot should be adjusted to run in series. Also the study revealed that the subsurface flow wetland was more suited for removing nitrate/nitrite than ammonia and a surface flow wetland may be more efficient at removing ammonia.

The first recommendation would be to make the pilot a three step treatment process, with the first step being a subsurface flow wetland, followed by a NMF and then the last step being a surface flow wetland. This change in treatment steps is recommended to better address the major contaminates of concern, ammonia, oil and grease, and PCBs. The purpose of the subsurface wetland would be to reduce pollutant loadings such as oils and suspended solids that may cause the NMF to blind. The NMF would still be utilized as a filter for PCBs and would still be operated as an up-flow unit. The effluent from the NMF could then be passed through a surface flow wetland to remove ammonia from leachate. The flow rate should be determine by the size of the final subsurface wetland and the time required for it to remove the high levels of ammonia at the minimum calculated first order reaction rate constant. The new pilot should be sampled for the same parameters as the current pilot and ran for an entire year. If successful, data gained from this pilot could then be used to design a full scale system.

For the development of NMF as an alternative to removing low levels of PCBs form wastewater, it is recommended that guidelines be developed for operation of pilots, to better understand the removal process. Each of the pilots operated by Alcoa EHS Technology Group has been a different size, shape, with varying flow rates, media and had loading rates. Developing guidelines on how to design, operate, and sample NMFs will help to better refine this technology. These guidelines should include a method for determining the adsorption capacity of the compost and how it changes during long term operation. Also, in large scale NMFs, the hydraulics should be closely monitored and tracked along with media consolidation to better understand how the media changes during operations. Data gained from more defined guidelines and long term operation of pilot NMF will help to refine the design parameters of this technology. This data will in- turn, prove that at NMF is an option for PCB treatment and coupled with CTWs can a very successful, low cost, long term treatment option.

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